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Validation and Improvement of EPA (Environmental Protection Agency) Reference Method 25 - Determination of Gaseous Nonmethane Organic Emissions as Carbon

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VALIDATION AND IMPROVEMENT OF EPA REFERENCE METHOD 25 - DETERMINATION OF GASEOUS NONMETHANE ORGANIC EMISSIONS AS CARBON

by

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The U.S. Environmental Protection Agency Reference Method 25 measures the total gaseous nonmethane organics as carbon in source emissions. Both laboratory and field studies were conducted to evaluate this method. Tested were the effectiveness of a commercial nonmethane organic analyzer, Byron Model 401, and the sample collection and conditioning system used. Two field tests at a textile plant and a plywood veneer plant were conducted using identical dual sampling trains. Various modifications are recommended to improve the method.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessing environmental monitoring technology and systems; implementing Agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise, and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

This investigation was conducted at the request of the Office of Air Quality Planning and Standards. A source test method for the measurement of total gaseous nonmethane organic substances as carbon was studied. The work was carried out to answer certain questions that arose because the method often produced inaccurate and imprecise results. For these reasons, the present investigation included a study of operating characteristics and the efficiency of components in the sampling system as well as some of the analytical processes. Both laboratory and field investigations were conducted.

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ABSTRACT

The U.S. Environmental Protection Agency Reference Method 25 measures the total gaseous nomethane organics as carbon in source emissions. Both laboratory and field studies were conducted to evaluate this method. Tested were the effectiveness of a commercial nonmethane organic analyzer, Byron Model 401, and the sample collection and conditioning system used. Two field tests at a textile plant and a plywood veneer plant were conducted using identical dual sampling trains. Various modifications are recommended to improve the method.

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ABBREVIATIONS AND SYMBOLS

C_2	--	ethane, ethylene, or acetylene
C_c	--	condensible organic concentration
EPA	--	U.S. Environmental Protection Agency
FID	--	flame ionization detector
GC	--	gas chromatography/chromatograph
LC	--	leak check
NDIR	--	nondispersive infrared
NMO	--	nonmethane organics
ppmC	--	parts per million as carbon
RSD	--	relative standard deviation
s_d	--	pooled standard deviation
VOC	--	volatile organic compounds
V_s	--	sample tank volume
V_v	--	vessel volume

SECTION 1

INTRODUCTION

On October 5, 1979, under Section 111 of the amended Clean Air Act, the U.S. Environmental Protection Agency (EPA) proposed standards limiting the emissions of volatile organic compounds (VOC) from new, modified, and reconstructed automobile and light-duty surface-coating operations within assembly plants (1). The standards were based on EPA's determination that such emissions contribute significantly to air pollution by acting as precursors for formation of ozone and other photochemical oxidants that impact adversely on health and welfare.

The standard included a method for measuring VOC emissions, EPA Reference Method 25.* According to Method 25, an emission sample is withdrawn from the source stack through a chilled condensate trap and into an evacuated sample tank. The total gaseous nonmethane organics (NMO) are then determined by combining the results obtained from separate analyses of the condensate trap and sample tank fractions. The organic contents of the condensate trap are oxidized and quantitatively collected in an evacuated vessel, and an aliquot of the resulting CO_2 is reduced to methane and measured by a flame ionization detector (FID). An aliquot of the gas collected in the sample tank is introduced into a gas chromatographic (GC) system to separate the nonmethane organics from carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4). After this separation, the NMO are oxidized to CO_2, reduced to CH_4, and measured by an FID. In this way, variations in FID response to different compounds are eliminated, and all carbon is measured as methane.

Application of the method revealed deficiencies that affect the accuracy and reproducibility of the results (4). As a result, the present investigation was undertaken to systematically evaluate EPA Reference Method 25 and to recommend further modifications to improve the accuracy, precision, and reliability of the data collected. In addition to a laboratory evaluation, two field tests of the method were conducted to determine the quality of the data that can be expected using Method 25.

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*The method was adapted originally from a procedure introduced by Salo et al. (2). EPA Reference Method 25 was modified in 1980 (3); a copy is presented in Appendix A.

SECTION 2

CONCLUSIONS

Laboratory evaluations of EPA Reference Method 25 revealed that recoveries of organic gases exceeded 90 percent when several standardized mixtures of these gases in air or nitrogen were analyzed. At first, poor precision was encountered in field testing. When dual trains were employed to sample a fabric finishing plant effluent stream, a 31-percent relative standard deviation (RSD) was obtained for the pooled values. These results prompted modification of the sampling trains, improvement of the condensible organics recovery procedure, and introduction of a sampling train dead volume correction. When these techniques were employed in the sampling of the effluent from a plywood veneer dryer using dual sampling trains, the pooled values yielded an 8-percent RSD.

The Byron Model 401 analyzer showed excellent linearity for a variety of organic compounds with the linear range extending over three orders of magnitude in some instances. However, the response to samples of different compounds containing equal ppmC was found to be different. Incomplete oxidation of organic compounds to CO_2 within the analyzer and peak tailing are among the many causes that may have contributed to the unequivalent response. This response variability is expected to result in inaccuracies for measurement of the volatile portion of the sample that is not captured by the condensate trap and ends up in the sample tank. The variability of response, however, should have no effect on the precision of results for samples collected via the dual sampling trains.

SECTION 3

DESCRIPTION OF APPARATUS

SAMPLING SYSTEM

The sampling system consisted of a 0.125-in. o.d. stainless steel probe, a condensate trap, a flow control system, and a sample tank. The condensate traps were constructed of 316 stainless steel according to the specifications shown in Figure 1. The flow control system consisted of a NUPRO toggle-operated bellows seal valve for quick shutoff, a NUPRO fine-metering valve, a 0-to-760-mm-Hg vacuum gauge, and a NUPRO bellows seal valve on the sample tank (Figure 2). The stainless steel sample tanks had a nominal volume of 2 L and the inner surfaces of the tanks were treated electrochemically to achieve surface inertness.

A Sargeant-Welch Model 8810 vacuum pump was used to evacuate the sample tanks and a Heise bourdon tube pressure vacuum gauge was used to measure the tank's absolute pressure.

ANALYTICAL SYSTEM

A Byron Model 401 total emission analyzer was used to measure NMO from the sample tank and CO_2 from the condensate trap oxidation. The instrument was designed to measure total hydrocarbons, nonmethane hydrocarbons (NMHC), CH_4, CO, and CO_2. A schematic representation of the operation of this instrument is shown in Figure 3. Briefly, the gas sampling loop is filled by flowing sample gas under pressure through the loop; the loop contents are injected onto a chromatographic stripper column consisting of silicone oil on solid support and porous polymer beads using zero air as the carrier. Carbon monoxide, CO_2, CH_4, acetylene, ethane, and ethylene elute into a separation column. Methane and CO elute from the separation column. The stripper column is backflushed into an oxidation catalyst where any organics are oxidized to CO_2, which is then mixed with hydrogen and passed through a reduction catalyst for conversion to CH_4 and measurement by an FID. Carbon dioxide elutes from the separation column and undergoes the same oxidation-reduction measurement steps. Subsequently, two-carbon compounds elute and are converted first to CO_2 and then to CH_4 and are measured. Finally, the CH_4 and CO are released from the storage column and measured separately after oxidation and reduction.

Detector output was monitored by a Linear Instruments Corporation strip chart recorder, and the output signal was integrated electronically with a Spectra Physics Minigrator.

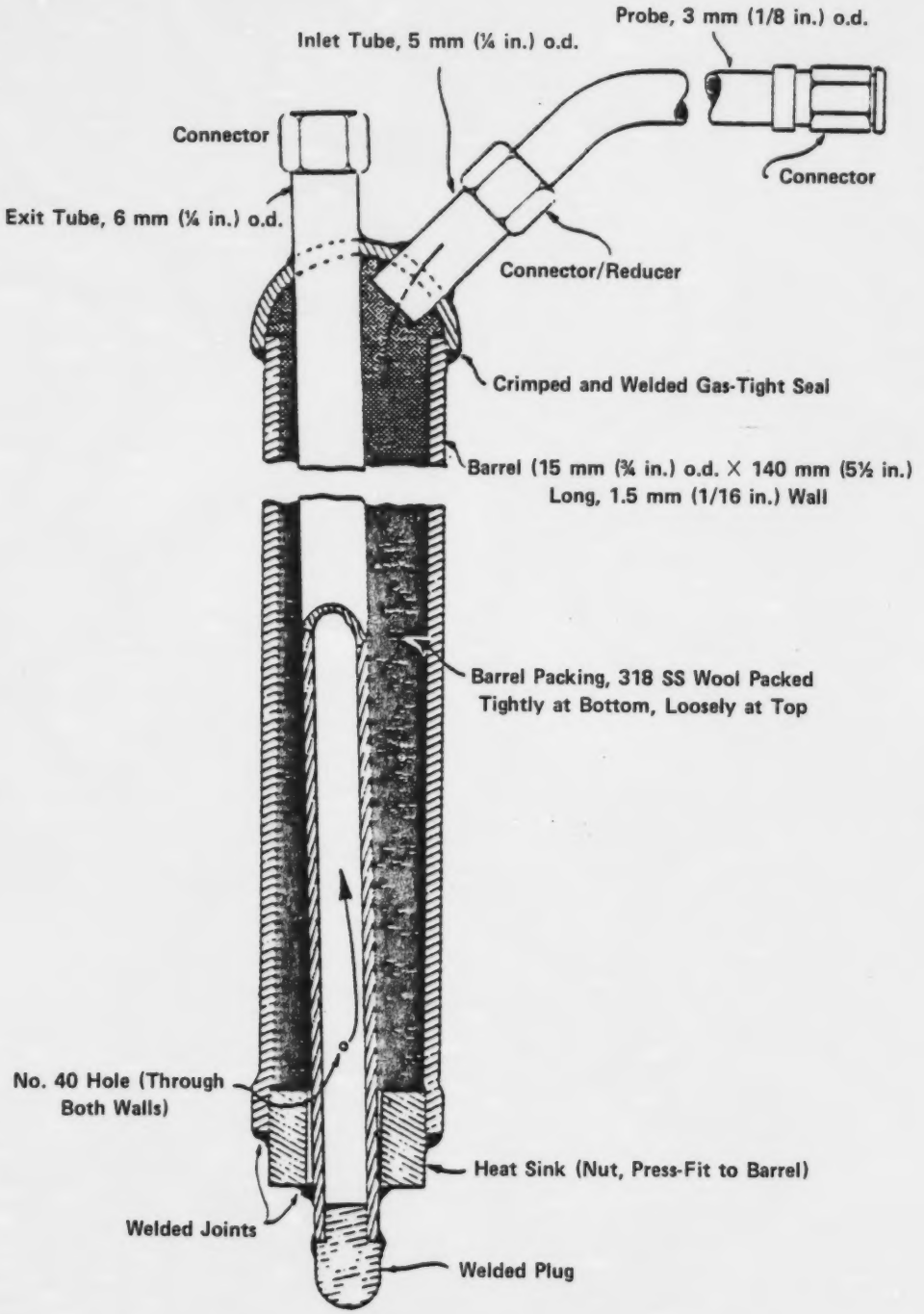
Probe, 3 mm (1/8 in.) o.d.
Inlet Tube, 5 mm (¼ in.) o.d.
Connector
Connector
Exit Tube, 6 mm (¼ in.) o.d.
Connector/Reducer
Crimped and Welded Gas-Tight Seal
Barrel (15 mm (¾ in.) o.d. X 140 mm (5½ in.) Long, 1.5 mm (1/16 in.) Wall
Barrel Packing, 318 SS Wool Packed Tightly at Bottom, Loosely at Top
No. 40 Hole (Through Both Walls)
Heat Sink (Nut, Press-Fit to Barrel)
Welded Joints
Welded Plug
Material: Type 318 Stainless Steel

Figure 1. Condensate trap specifications.

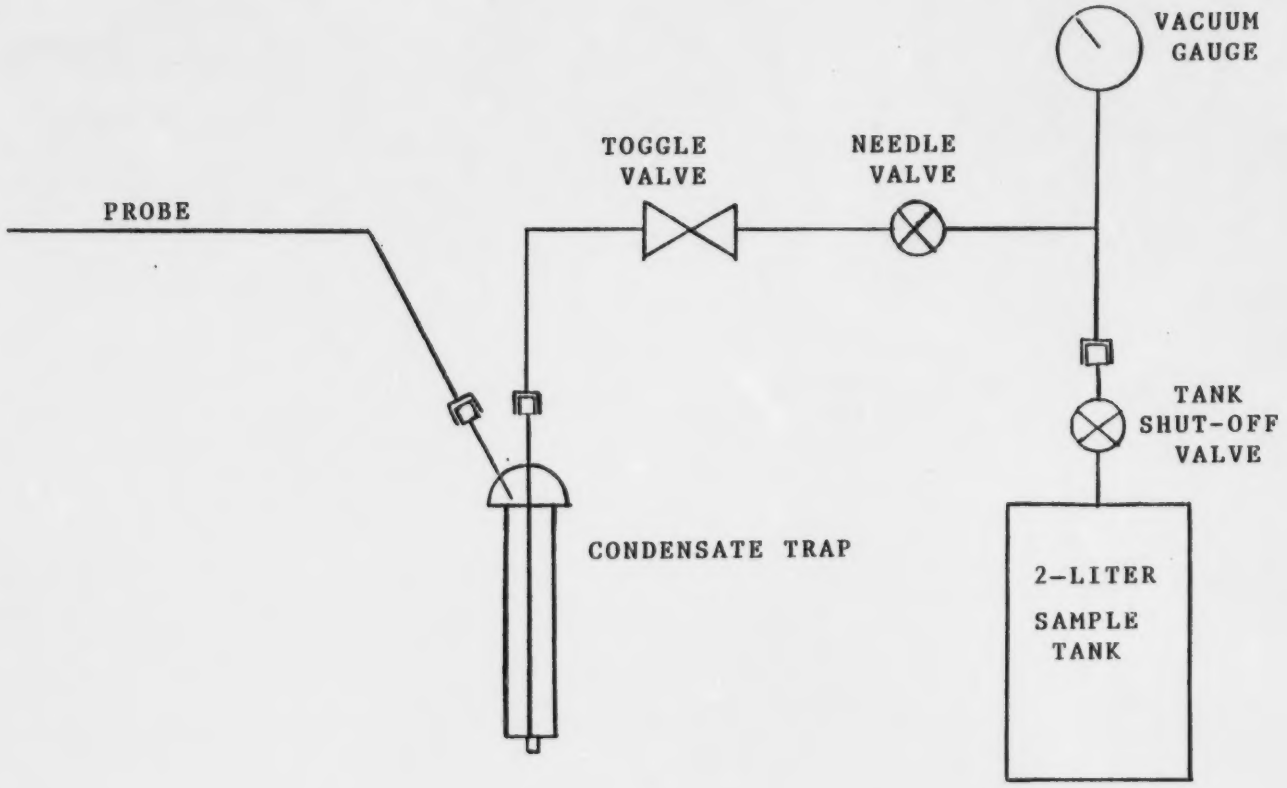

Figure 2. Sampling train.

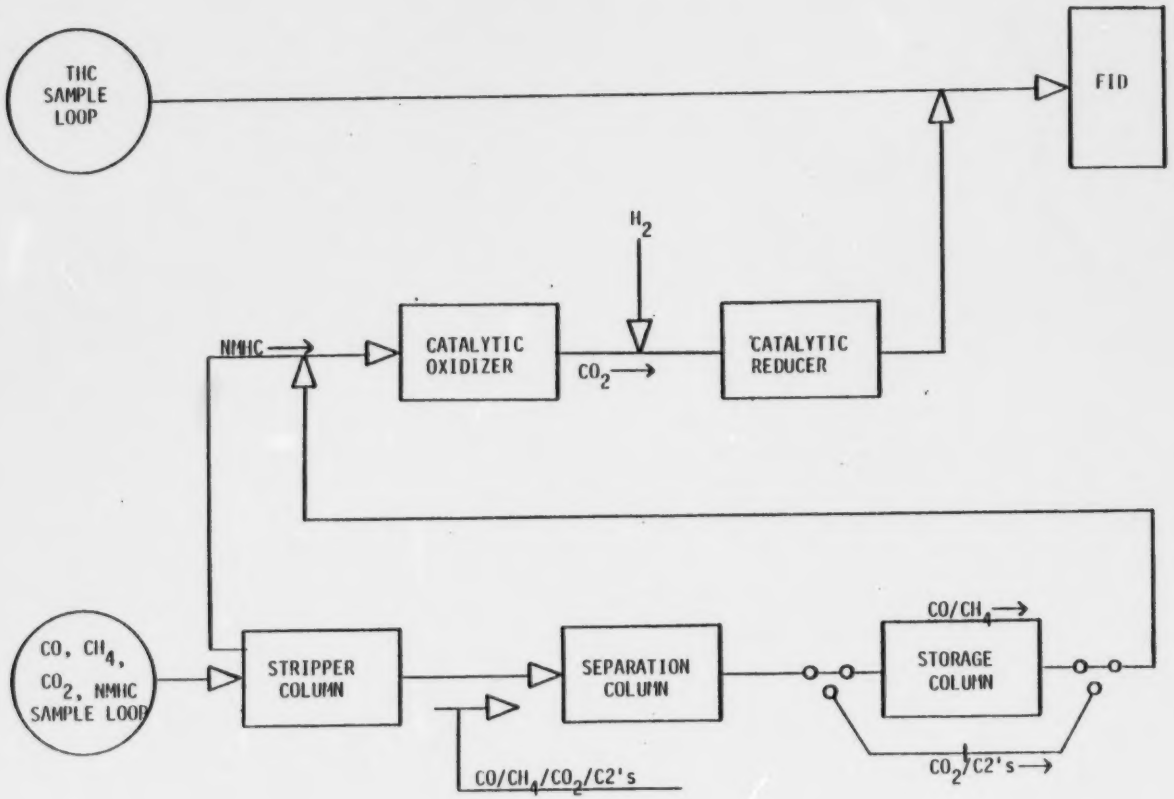

Figure 3. Byron 401 analyzer.

CONDENSATE RECOVERY AND CONDITIONING SYSTEM

The system used for recovery and conditioning of the trapped organics consisted of a heat source, oxidation catalyst, nondispersive infrared (NDIR) analyzer, intermediate collection vessel, and associated flow control devices. The heat source was an electrically heated tube furnace capable of heating to 700° C. The oxidation catalyst consisted of 0.375-in.-o.d. × 14-in.-long inconel tubing packed with 8 in. of hopcalite oxidizing catalyst and was operated at 800° C in a tube furnace. The construction of the water trap, out of 316 stainless steel, is the same as that of the condensate traps. The NDIR detector was a Horiba PIR-2000 with full-scale ranges of 2000 ppm, 5000 ppm, and 1 percent. The intermediate collection vessel was identical to the sample tanks. The vacuum gauge was a Heise bourdon tube gauge with a 0-to-130-in.-Hg range and 0.1-in.-Hg scale divisions. The carrier gas consisted of 5 percent oxygen in nitrogen containing less than 1 ppmC. The auxiliary O_2 was zero-grade oxygen containing less than 1 ppmC. A schematic of the system is shown in Figure 4.

Test gases were obtained from Scott Environmental Technology. The mixtures of the compounds of interest in either air or nitrogen were contained in aluminum or steel cylinders. They were certified by the manufacturer and remeasured at the Research Triangle Institute (RTI). Several analyses were rechecked at EPA. Several National Bureau of Standards Standard Reference Materials (NBS-SRMs) were also employed, namely, propane in air, CO in nitrogen, CO_2 in air, and CH_4 in air.

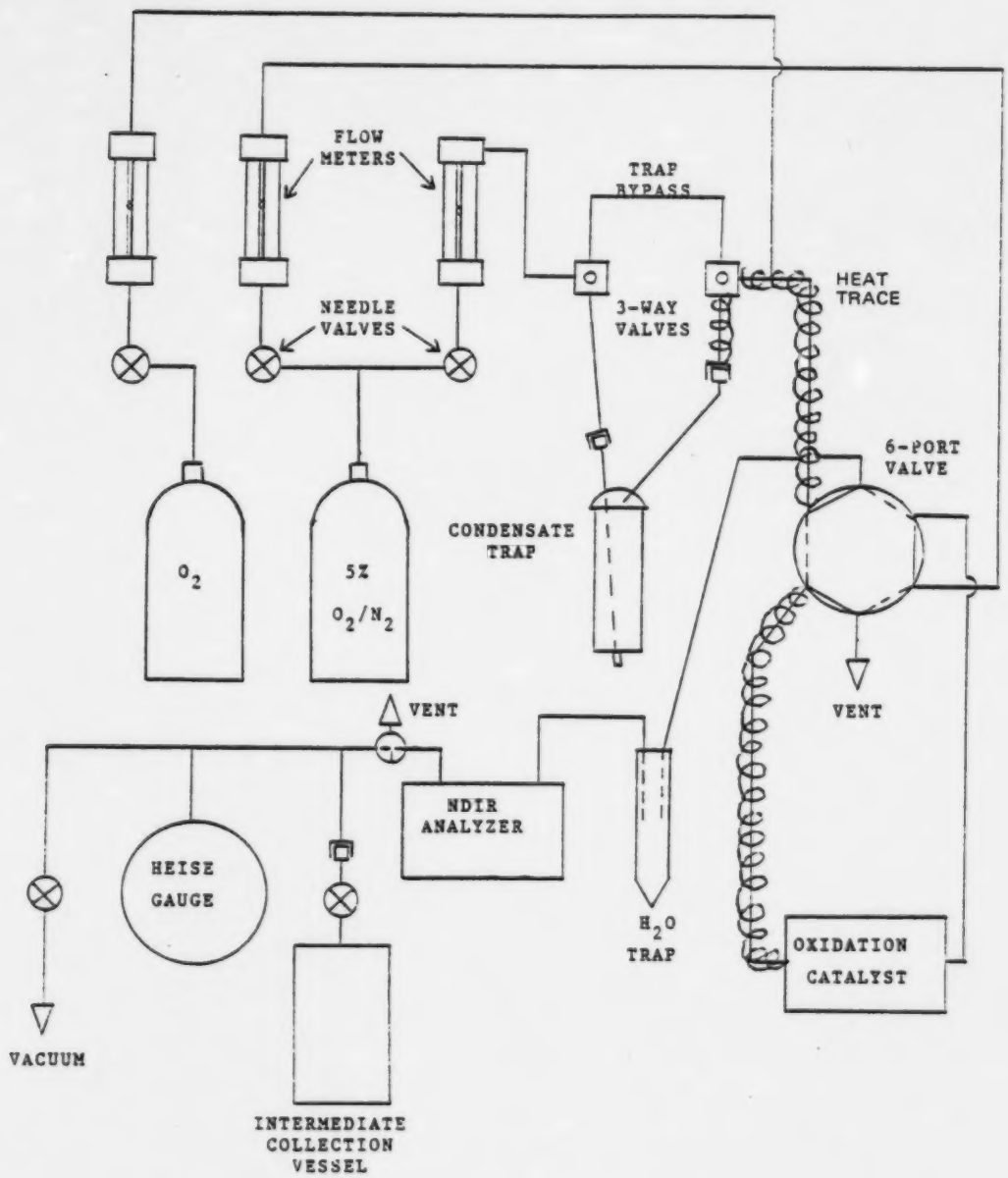

Figure 4. Condensate recovery and conditioning system.

SECTION 4

LABORATORY EVALUATION

SAMPLING SYSTEM

The accuracy and precision of the sampling system in collecting a sample quantitatively was verified by sampling 603-ppmC propane in air flowing through a stainless steel manifold. Two separate samples yielded an average concentration of 602.2 ± 0.6 ppmC. This amount equals a recovery of 99.9 percent and an RSD of 0.08 percent.

One concern was the dilution of the sample by air in the condensate trap and other parts of the sampling system. The sampling procedure for Method 25 designates that the sample tank be evacuated before it is connected to the sampling train and the pressure is measured and recorded for use in the calculations. Subsequently, during the pretest leak check, the probe tip is plugged and the shutoff valve opened, allowing the air contained in the trap to enter the sample tank and increase the pressure before the actual sampling. After the probe tip is unplugged, ambient air reenters the trap. This volume of air is drawn into the sample tank when sampling begins and will dilute the stack gas.

To determine if the trap dead volume effect was significant, a sample was collected in which the condensate trap was filled with the gas under analysis before sampling began. Using this method, 98.2 percent recovery of a 603-ppmC propane sample was achieved. Sampling performed without taking precautions to flush the trap resulted in 96.6 percent recovery of the same 603-ppmC propane. Thus, with a 2-L sample tank, the trap dead volume produced less than a 2 percent error. The error would probably be even less if the tank volume were larger (e.g., 4 to 6 L), provided a larger sample were collected.

One area of concern is the use of Reference Method 25 to sample combustion source emissions that contain high concentrations of both CO_2 and water vapor, since CO_2 may dissolve in the water condensate and then be frozen in a solid solution or be physically entrapped in the ice that forms in the condensate trap. Such CO_2 trapped within the ice would not be released during the condensate recovery CO_2 purge, since the trap is maintained at dry ice temperature to prevent volatilization of organics. If the trap were heated and its organic contents oxidized, the entrapped CO_2 would also be released and an erroneously high VOC measurement would result.

An initial experiment was performed to measure the recovery of a relatively low concentration of CO_2 diluted in a high concentration water vapor matrix. A synthetic atmosphere containing 834 ppm CO_2 and 6.2 percent water vapor was established by mixing 10,000 ppm CO_2 with air that had been saturated with water vapor by flowing it through a heated bubbler. The water vapor concentration was monitored by an Environmental and Equipment Company (EG&G) dewpoint hygrometer. The concentration of CO_2 measured by drawing a sample from the heated manifold through a dry-ice-chilled condensate trap was 841.6 ppm (100.9 percent recovery). Future studies are planned in which higher levels of CO_2 and water vapor will be sampled and the condensate trap analyzed to determine the extent of the CO_2 interference.

ANALYTICAL SYSTEM

The two major parts of the analytical system--the Bryon Model 401 total emissions analyzer and the condensate recovery and conditioning system--were evaluated.

NMO Analyzer

Although the Byron Model 401 analyzer was found to produce a linear response for several compounds tested up to three orders of magnitude (Tables 1 and 2), it was found to be deficient in other aspects. The major problem was the unequal response to equal ppmC concentrations of different organic compounds. Initially, a 90-percent difference between propane and toluene response was found, with propane being higher. After servicing the instrument and replacing the reduction catalyst, a 41-percent difference between propane and toluene response was found, with propane response now being lower. Since the methanation catalyst had been changed, inefficient operation of the oxidation catalyst was suspected.

An oxidation catalyst identical in design to the one used in the Byron Model 401 was obtained and used externally in the oxidation of propane and toluene standard cylinder gases to investigate the reason for this variation in response. The catalyst test procedure consisted of flowing the gas at 150 cm^3/min through the oxidation catalyst into a stainless steel sampling manifold. A sample was then drawn into the Byron analyzer for component analysis. The chromatogram of the oxidation products of 59.7 ppmC propane in air showed NMO (C_2 as well as heavier) CO_2 and CO. A chromatogram of the products produced while oxidizing 128.1 ppmC toluene in air was similar, except that no C_2 compounds were seen. A 5.7-percent difference was detected between propane and toluene in the amount of CO produced per ppmC organic. The major differences, however, were in the production of C_2 compounds and CO_2 produced per ppmC organic (254.4 CO_2 area counts/ppmC propane, 300.7 CO_2 area counts/ppmC toluene).

Although the flow experiment described above does not truly simulate the actual oxidation characteristics in the Byron instrument, the unequal response between propane and toluene could be explained, at least qualitatively, by two factors. First, the C_2 produced during the oxidation of

TABLE 1. VARIATION OF THE BYRON MODEL 401 ANALYZER RESPONSE TO VARIOUS ORGANIC COMPOUNDS

Compound	Concentration range, ppmC	Relative response*
Trichloroethylene	40	603
Ethylene	10 - 40,000	473
Methyl acetate	50 - 1,300	215
Ethane	600 - 1,400	608
Freon 113	30	652
Carbontetrachloride	20	859
Isopropyl alcohol	300	365
Decane	260	864
Acetyl acetone	400	428
Nonane	455	825
Amyl acetate	350	787
Tetrahydrofuran	150 - 500	436
Tetrahydropyran	60	451
Naphthalene	25	721
Propane	60 - 9,000	470
Toluene	60 - 128	805
Hexane	330	429
Methanol	100	272
Propylene	30	463
Benzene	600	647

*Area counts/ppmC.

TABLE 2. LINEARITY STUDY

Compound	ppmC	Average response factor	Percent Δmean
Propane	59.7	467.1	-0.7
	603.0	480.5	+2.1
	9,150.0	463.8	-1.4
Benzene	49.2	677.3	+4.6
	58.2	672.4	+3.8
	390.0	665.7	+2.8
	468.0	639.6	-1.2
	798.0	645.8	-0.3
	2,088.0	639.3	-1.3
Ethylene	9.5	492.2	+4.0
	39.2	487.8	+3.0
	624.0	469.5	-0.8
	6360.0	498.2	+5.3
	40,912.0	432.6	-8.6
Propylene	14.8	413.4	+4.6
	60.0	395.5	0.0
	894.0	382.9	-5.2
	2,049.0	390.2	-1.3
Methyl acetate	52.5	215.1	0.0
	963.0	215.1	+0.1
	1,347.0	215.1	0.0
Ethane	590.0	585.3	-3.7
	1,194.0	658.1	+8.3
	1,428.0	579.9	-4.6

propane was not reduced efficiently to methane by the reduction catalyst before passing to the FID. Second, the CO was not converted completely to methane. Schwenk et al. (6) have shown that at the temperature at which CO_2 is completely converted to methane, CO disproportionates into CO_2 and elemental carbon, and that this latter substance is relatively unreactive. Since more CO_2 per ppmC was produced from toluene, its response would then be higher than propane. The actual 42 percent difference between the response of propane and toluene probably is due to a combination of factors, but the incomplete oxidation of the organics to CO_2 during the NMO backflush appears to be a major contributor.

The responses of several organics were determined for the Byron analyzer and are shown in Table 1. This variability in per-carbon response to different organics presents a problem when these organics are not trapped in the Method 25 condensate trap. Trapping would allow conversion to CO_2 during condensate conditioning and subsequent measurement against a standard CO_2 gas. However, since propane is used as a standard for the tank portion of the sample, the response variability may lead to significant errors.

Another problem with the Byron Model 401 was the severe tailing of some compounds during the NMO backflush. One probable reason for the tailing of compounds such as toluene, hexane, and methanol is that an air carrier gas is required (as per design for proper operation) in the instrument instead of helium or nitrogen. The air could interact with the compound on the column, presumably via oxygen/adsorption site competition. Peak tailing results in peak integration problems, which could account for a portion of the response variability. Other reasons for tailing could be excessive volume or improper sample inlet geometry.

As a part of the Byron Model 401 evaluation, the Initial NMO Analyzer Performance Test detailed in Method 25 was completed with the exception of the oxidation catalyst efficiency test, since evidence of poor catalyst efficiency already had been obtained.

Nitrogen dioxide (NO_2) and sulfur dioxde (SO_2) were found not to interfere in Byron 401 NMO analysis. When a gas sample containing 100 ppm CO, 200 ppm NO_2, and 500 ppm SO_2 was measured, 99.6 ± 1.2 ppm CO was found. Further, no response was noted in the CH_4 or NMO windows.

The results of the analyzer linearity study and NMO calibration are shown in Table 2. Although the response factors varied considerably for the various compounds listed in Table 2, each factor remained relatively constant over a wide range of concentrations. The instrument linearity was acceptable, since the average response factor of each propane calibration gas was within 5 percent of the overall mean value. The RSD for each set of triplicate injections was less than 5 percent.

Table 3 shows the results of the reduction catalyst efficiency check and CO_2 calibration. The overall mean response factor is 555.1 area counts per ppm. The linearity of response to CO_2 was acceptable. The overall

TABLE 3. CARBON DIOXIDE CALIBRATION

CO_2, ppm	Average response factor	Percent RSD	Percent Δmean
57.3	558.1	0.24	0.54
509.0	574.3	0.40	3.46
10,000.0	532.9	0.09	4.00

oxidation/reduction catalyst efficiency was not acceptable, since a 15-percent difference in response was found between CO_2 and propane. It is unclear whether this difference in response is due to reduction catalyst deficiencies, the oxidation catalyst problems previously described, or a combination of both.

The NMO system blank value was determined to be less than 10 ppmC.

The system performance check, which consists of measuring the responses to hexane, toluene, and methanol, failed because of the variation in response factors shown in Table 1. The measured NMO value for each gas using propane as the calibration standard should be within 12 percent of the expected value.

Condensate Recovery and Conditioning System

The first step in the evaluation of the condensate recovery and conditioning system was to complete the initial performance test as outlined in the Federal Register (Appendix A).

The carrier gas/auxiliary oxygen blank was checked by setting equal flow rates of the two gases and by filling an evacuated sample tank with the trap switching valves in the bypass position and the oxidation catalyst in-line. The tank was analyzed for CO_2 and found to contain 6.1 ppm, which is below the allowable limit of 10 ppm.

The oxidation catalyst efficiency was checked by flowing 9,850 ppm methane in air through the catalyst and into an evacuated sample tank. The tank was analyzed for CO_2 and found to contain 9,511 ppm (3.4 percent difference from methane concentration). Thus, the catalyst efficiency was within the allowable limits (95 to 105 percent).

So that the system performance check could be completed, a regular condensate trap was fitted with a 1/4-in. stainless steel tee and rubber septum to allow liquid injections of hexane and toluene into the trap. The results of this test are shown in Table 4.

TABLE 4. SYSTEM PERFORMANCE CHECK

Compound	Microliters injected	Percent recovery
n-Hexane	100.0	82.8
n-Hexane	9.0	96.4
Toluene	100.0	81.1
Toluene	9.0	94.0

The lower recovery of the 100-µL injections of each compound may be due to the nonlinear response of the Byron NMO analyzer at very high CO_2 concentrations. Approximately 32,000 ppm CO_2 was produced from 100 µL of hexane, and about 45,000 ppm CO_2 from 100 µL of toluene.

Gaseous samples of hexane and toluene were also tested to determine the accuracy of the liquid condensate recovery and conditioning system and the sample tank fraction measurements. The sampling system shown in Figure 2 was used. When sampling 332.4 ppmC hexane in air from a stainless steel manifold, 91 percent of the sample was recovered with 20 percent of that recovered being trapped in the dry ice trap. Two samples of 2,799 ppmC toluene in air were measured at 2,696 ± 69.9 ppmC (RSD = 2.6 percent). This amount equals 96.3 percent recovery with 78 percent of the toluene being trapped in the dry ice trap.

SECTION 5

FIELD EVALUATION

The first field test of Method 25 was conducted at a textile dyeing and finishing plant. Four sets of dual samples were collected from a stack used to vent emissions from the drying of polyester fabric. Figure 5 is a diagram of the process with the sampling point identified.

The second field test was performed at a plywood veneer drying plant. Four sets of dual samples were collected from a stack containing the exhaust from a manual-feed plywood veneer drying process. This test evaluated the applicability of Method 25 to sources containing high concentrations of water vapor. Figure 6 shows a diagram of the process. The data sheets for field tests I and II are included in Appendix B.

FIELD TEST I

Sampling

The sample tank pressures were measured initially with a Heise gauge before the sampling trains were assembled. The trains were then assembled, and each condensate trap was immersed in dry ice. A pretest leak check was performed by plugging the probe tip, opening the shutoff valve, and monitoring the system pressure for 10 min. After a satisfactory leak check, the probes were unplugged, fastened together, and placed into the stack sampling port. The flow controllers, which had been calibrated in the laboratory, were set at the desired sampling rate. After the initial guage vacuum and the time were recorded, the shutoff valves were opened to begin sampling. During the first run, the sampling train B average flow rate was approximately 50 percent faster than sampling train A. In the second run, sampling train B was 25 percent faster than sampling train A. The average sampling rates were matched for runs #3 and #4. The condensate trap on train A in run #4 was immersed in ice water instead of dry ice.

The gauge vacuum was recorded at 5-min intervals until sampling was completed. A posttest leak check was performed by plugging the probe tip, opening the shutoff valve, and monitoring the system pressure for 10 min. After a successful leak check, the condensate trap, sample tank, and probe were disconnected from the flow metering system, and all fittings were tightly capped.

Analysis

The first step in NMO analysis was to purge the condensate trap of CO_2 and pressurize the sample tank. The condensate trap was repacked in dry

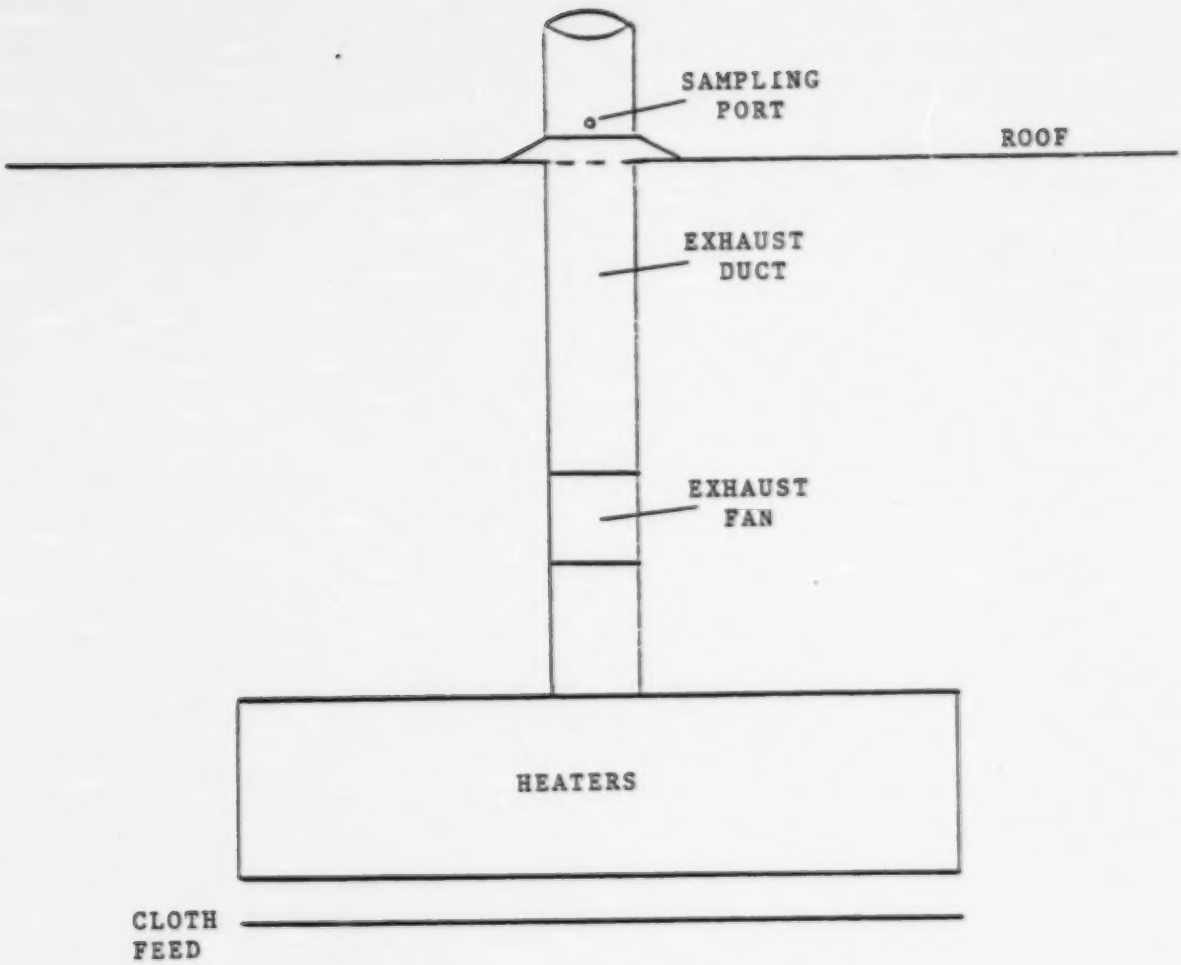

Figure 5. Field sampling diagram.

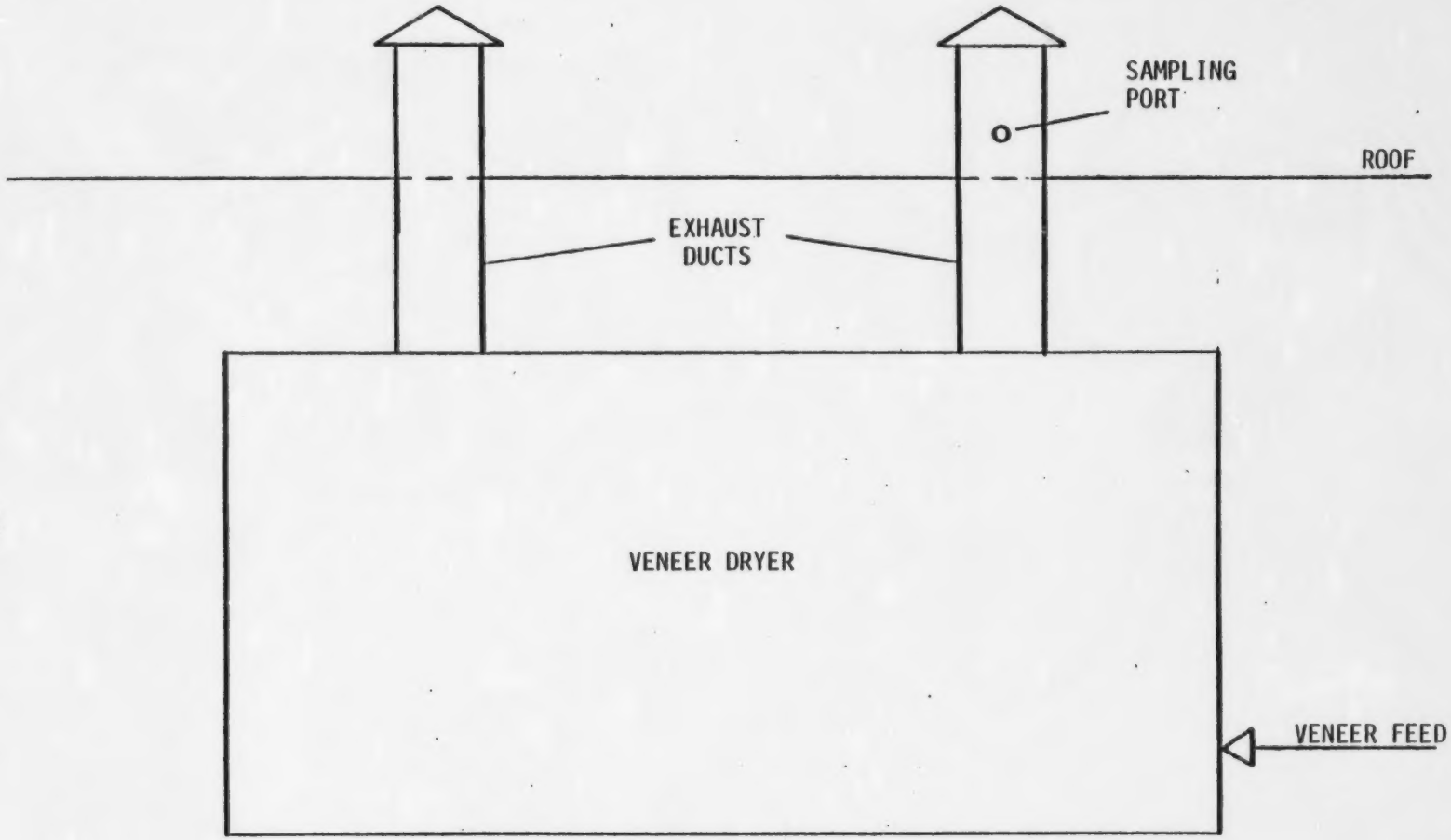

Figure 6. Plywood veneer dryer.

ice and allowed to cool for 15 min before it was opened and attached to the condensate recovery system. The matching sample tank was attached to the system to collect the purged CO_2 and pressurized. The system valving was set so that the trap contents were purged into the sample tank while the CO_2 was monitored with an NDIR. When all of the CO_2 had been purged, the trap was bypassed and the sample tank pressurized to approximately 800 mm Hg gauge pressure.

The sample tank was analyzed for NMO by triplicate injection into the Byron analyzer. After analysis, the sample tank was evacuated and reattached to the condensate recovery system for use as the intermediate collection vessel. The carrier gas flow was directed through the condensate trap, the dry ice was removed, and the trap was placed in a tube furnace that was slowly heated to 500° C. A carrier gas flow of 30 cm^3/min of 5 percent oxygen in nitrogen was used to flush the trap. The carrier gas stream was mixed with 35 cm^3/min of pure oxygen before being passed to the oxidation catalyst. The NDIR was monitored, and the recovery was considered complete when the meter reached a minimum deflection. The intermediate collection vessel was pressurized to at least 800 mm Hg gauge pressure and analyzed for CO_2 by triplicate injection into the Byron analyzer.

Results

The results of the field sample analysis are shown in Table 5. The percent difference between NMO determined with sample train A and with sample train B for each run is: run #1--48.5 percent; run #2--19.5 percent; run #3--44.2 percent; and run #4--2.7 percent. The imprecision of the dual samples for the first three runs may have resulted from a leaking toggle shutoff valve that was not discovered until the end of run #3. During the normal leak-check procedure specified in the Federal Register (Appendix A), this leak would not be discovered because the probe end is plugged. However, in the process of properly inserting the dual probes into the stack, it would allow leakage into the trains. Another probable

TABLE 5. RESULTS FOR FIELD TEST I

	Sample train A (ppmC)				Sample train B (ppmC)			
	Run #1	Run #2	Run #3	Run #4	Run #1	Run #2	Run #3	Run #4
Noncondensible organics	8.7	<3.0	4.3	159.6	7.7	3.5	<3.8	55.6
Condensible organics	627.1	243.7	641.5	578.7	319.9	192.7	360.2	703.2
NMO	635.8	243.7	645.8	738.3	327.6	196.2	360.2	758.8

cause for the imprecision of the data was that a constant flow rate may not have been maintained over the entire duration of the run because of an increase in sample tank pressures, since the needle valves that were used to control the flow do not give a visual indication of the constancy of the flow rates. However, run #4 gave good precision after the toggle valve problem was corrected even though an icewater trap was used for sample train A and a dry ice trap for sample train B. The results for run #4 show that the sample tank from sample train A contained a higher fraction of the total organics than sample train B. This difference was due to the use of an ice water bath for trap cooling instead of dry ice on sample train A.

FIELD TEST II

Sampling

Several modifications were made to the sampling trains for this test. Because it was known a priori that the veneer dryer exhaust could contain up to 30 percent water vapor, a second condensate trap immersed in ice water was added in front of the condensate trap immersed in dry ice. The purpose of this additional trap was to condense water vapor before it entered the dry ice trap where plugging from ice formation could occur. The bellows seal toggle valve used as a quick shutoff valve was removed from the train because it leaked during the first field test. The needle valve used for flow control was replaced with a rotameter and integral needle valve. In addition, each probe was fitted with a particulate filter that consisted of a 0.124-in. Swagelok union packed with glass wool. Figure 7 is a diagram of the modified sampling train.

After the initial tank pressures were measured, the sampling trains were assembled and the condensate traps immersed in ice water and dry ice. The leak-check scheme was varied for some of the runs to determine the effect of sample train dead volume on the sampling. In run #1 and run #2, both pretest and posttest leak checks of the entire sampling train were performed by plugging the probe tip, opening the tank shutoff valve, and monitoring the system pressure for 5 min after the rotameters indicated that the pressure had equilibrated between the sample tank and the rest of the train. In run #3, only a pretest leak check of the entire sampling train was performed. In run #4, a pretest leak check was performed by closing the rotameter needle valve, opening the sample tank shutoff valve, and monitoring the pressure for 5 min. The probe side of the needle valve was not checked in this final test, since it is essentially at atmospheric pressure during the sampling.

After a satisfactory leak check, the probes were unplugged, fastened together, and placed into the stack sampling port. To begin sampling, the tank shutoff valves were opened and the flow adjusted to the desired sampling rate. Table 6 gives details of the sampling rate and sampling time for each train during each run. Identical sampling rates were used for the two trains for the first three runs. A factor of 2 difference was used for the flow rates of the two trains for the fourth run to test method ruggedness. The gauge vacuum was recorded at 5-min intervals, and periodic adjustments

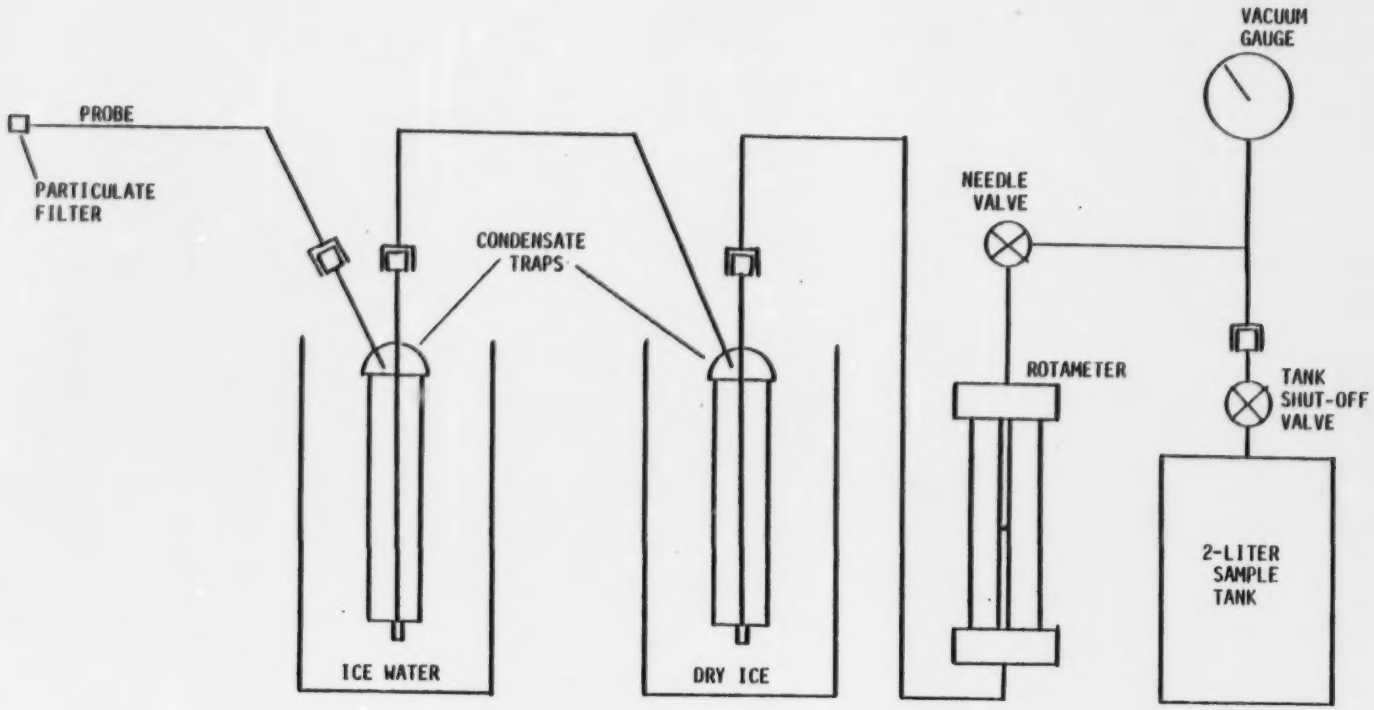

Figure 7. Modified sampling train.

TABLE 6. SAMPLING SCHEME FOR FIELD TEST II

Run #	Sampling train A		Sampling train B	
	Flow rate, cm^3/min	Sample time, min	Flow rate, cm^3/min	Sample time, min
1	25	20	25	20
2	25	20	25	20
3	25	30	25	30
4	20	30	40	30

were made in the rotameter needle valve to maintain a constant flow rate. After sampling was complete, the condensate traps, sample tank, and probe were disconnected from the flow metering system, and all fittings were tightly capped.

Analysis

The first step in NMO analysis was to purge each condensate trap of CO_2 and gaseous organics and pressurize the sample tank. Each trap was immersed in the same coolant used during sampling and allowed to cool for a minimum of 15 min before being opened. Each trap was then separately attached to the condensate recovery system and purged with 5 percent oxygen in nitrogen at 50 cm^3/min for 5 min while the NDIR response was monitored. The sample tank was pressurized to approximately 800 mm Hg gauge pressure and analyzed for NMO by triplicate injection into the Byron analyzer. After analysis, the sample tank was evacuated, filled with zero air, and re-evacuated for use as the intermediate collection vessel.

After attaching the tank to the condensate recovery system, a carrier gas flow of 85-cm^3/min 5 percent oxygen/nitrogen was directed through the trap, the ice water bath removed, and the trap placed in a tube furnace that was slowly heated to 500° C. An auxiliary oxygen flow of 15 cm^3/min was added to the trap flow before introduction to the oxidation catalyst. These flows are somewhat different than those used in the analysis of the first field test samples. The major improvement is that more carrier gas is flowed through the trap to prevent carbonization of the organics. The NDIR was monitored while the trap was baked and the attached probe was heated with a heat gun. The intermediate collection vessel was pressurized to about 1,600 mm Hg gauge pressure and analyzed for CO_2 by triplicate injection into the Byron analyzer. After analysis, the tank was evacuated, filled with cleaned air, and re-evacuated for use in the recovery of the dry ice trap sample.

Results

The results of Field Test II are shown in Tables 7 through 10. Table 7 shows the results before any corrections were made for sampling train dead volume. Table 8 gives the corrected results. Tables 9 and 10 give the corrected noncondensible organic and condensible organic concentrations as well as NMO for each run for sample train A and sample train B, respectively.

The 19.1-percent difference between sample train A and sample train B results in run #1 could be attributed partially to a leak discovered (and corrected during the run) in sample train B. The actual volume sampled by train B is probably greater than 672 cm^3; however, the volume that entered the tank during the leak test cannot be estimated.

The improvement in the precision of run #4 when the results are corrected is a consequence of different volumes being sampled by train A and train B. The contribution of dead volume error to sample train B is less than train A because of the larger sample volume collected by train B. Although the precision of the other runs was not improved by making corrections for dead volume, the accuracy was low because the train dead volume biased the concentration. The basis for making corrections in the concentrations is given in Appendix C.

The effect of train dead volume on accuracy increases as the dead volume approaches the total volume sampled. In previous laboratory sampling of propane, only one trap was used and a 1,300-cm^3 sample was collected. In this case, the error was less than 5 percent. The train dead volume was sizable during Field Test II because two traps and a 10-ft sampling probe were used. Such a long probe was necessary to keep the sampling trains at a safe distance from the high temperature stack. Also, approximately half the total sample was collected, as in the laboratory evaluation. The errors ranged from 7 percent for run #4B to 25 percent for runs #1 and #2.

In both field tests, the concentration range was relatively small and a pooled standard deviation, s_d, was calculated for the data using the paired values and the formula

$$s_d = \sqrt{\Sigma d^2/2n} \quad .$$

where

d = the difference between the paired values and

n = the number of sampling runs.

Application of this formula to the results in Table 5 yielded an s_d value of 150 ppmC. When compared with the average value of the data, 488 ppmC, an RSD of 31 percent resulted. Similar calculations on the data in Table 8 led to the following values: s_d = 486; mean value = 5858; RSD = 8.3 percent.

TABLE 7. UNCORRECTED RESULTS FOR FIELD TEST II

Run #	V_s, cm^3	LC scheme[a]	NMO, ppmC	Percent difference
1A	672	1	4816.5	19.1
1B	672	1	3898.3	
2A	672	1	3487.3	9.7
2B	672	1	3862.3	
3A	836	2	4922.2	4.4
3B	836	2	4705.9	
4A	600	3	5549.3	10.4
4B	1200	3	6195.4	

[a]LC schemes:
1 = pretest and posttest leak check;
2 = pretest leak check;
3 = no leak check.

TABLE 8. CORRECTED RESULTS FOR FIELD TEST II

Run #	V_s, cm^3	NMO, ppmC	Percent difference
1A	500	6473.4	19.1
1B	500	5239.3	
2A	500	4686.9	9.7
2B	500	5190.9	
3A	664	6197.1	4.4
3B	664	5924.9	
4A	514	6477.8	2.9
4B	1114	6673.7	

TABLE 9. SAMPLE TRAIN A RESULTS FOR FIELD TEST II

ppmC	Run #1	Run #2	Run #3	Run #4
Condensible organics (ice water)	2369.5	842.2	1156.0	1170.0
Condensible organics (dry ice)	3752.0	3693.6	4153.8	4499.5
Noncondensible organics	351.8	151.2	887.4	808.2
NMO	6473.4	4686.9	6197.2	6477.8

TABLE 10. SAMPLE TRAIN B RESULTS FOR FIELD TEST II

ppmC	Run #1	Run #2	Run #3	Run #4
Condensible organics (ice water)	1301.1	1022.1	1033.8	894.1
Condensible organics (dry ice)	3323.4	3724.6	4213.9	5250.5
Noncondensible organics	611.8	444.2	677.2	529.1
NMO	5239.3	5190.9	5924.9	6673.1

The RSD obtained in the second field test is approximately one-quarter of the value obtained in the first test, demonstrating that the modified procedures, especially the modified leak check and the dead volume correction, were effective in improving the precision of the analysis.

SECTION 6

QUALITY CONTROL/QUALITY ASSURANCE

SAMPLING

Sample tanks were leak-checked and tested for background NMO in the laboratory before being used in field sampling or laboratory sampling of synthetic mixtures. All sample tanks were evacuated in the laboratory and in the field prior to use. Both pretest and posttest leak checks of the assembled sampling trains were performed. Dual sampling trains were used in all field sampling to determine the precision of the sampling. Condensate traps were baked at 500° C for 24 h to remove any contamination. All sample tanks, condensate traps, and probes were clearly marked with aluminum tags engraved with an identification number.

CONDENSATE RECOVERY AND CONDITIONING SYSTEM

An initial performance check, including a carrier gas and auxiliary oxygen blank, a catalyst efficiency test, and a system performance test, was performed prior to using the system.

A carrier gas blank test was performed daily while either laboratory or field samples were being analyzed.

ANALYSIS

An initial NMO analyzer performance test was completed including analyzer linearity check and NMO calibration, reduction catalyst efficiency check and CO_2 calibration, NMO system blank, and a system performance check.

The NMO blank value, CO_2 calibration, and NMO calibration were determined daily while laboratory or field samples were analyzed. All calibration gases were prepared by Scott Environmental and certified to ±2 percent.

CALIBRATION AND PERFORMANCE AUDITS

Samples of three different organic compounds were prepared in Tedlar bags by the EPA project officer and delivered for analysis by Method 25. Table 11 shows the analysis results of each sample.

TABLE 11. PERFORMANCE AUDIT RESULTS

Compound	Actual concentration ppmC	Measured concentration ppmC
Acetone	325.8	296.7
Allyl alcohol	168.0	156.6
Formic acid	286.0	228.1
Formic acid	80.0	102.0
Formic acid	255.0	372.0

The problems with formic acid may be due to carbonization of the sample during condensate trap bake-out. This result was evidenced on the first two samples by prolonged NDIR response (~ 2 hours) after the trap was heated.

SECTION 7

RECOMMENDATIONS

APPARATUS MODIFICATIONS

Many of the problems with the Byron Model 401 analyzer might be alleviated to some extent by constructing an improved NMO analyzer. First, using only one column in the Byron Model 401 instead of three may substantially reduce the peak tailing problems by reducing the dead volume. Second, a more efficient catalyst, such as the hopcalite oxidizing catalyst used in the liquid condensate recovery and conditioning system instead of the proprietary catalyst used in the Byron instrument may solve the problem of response variability associated with incomplete oxidation of organics. Finally, an inert carrier gas such as helium or nitrogen used in the chromatographic portion of the analyzer instead of air may result in reduced interaction with the column material. Figure 8 shows the design of the improved NMO analyzer. A 60/80 mesh Porapak-N (Waters Associates) column would be used to separate the NMO from CO_2 and other gases. The column would first elute CO_2, then the NMOs could be backflushed out of the column into an oxidation-reduction system and finally into an FID. This design would be much simpler than that shown in Method 25 (Appendix A).

Also recommended is the use of a Heise bourdon tube pressure gauge in place of the U-tube mercury manometer. The Heise gauge's advantages include ease of use, portability, and ruggedness, and it is adequately accurate for making sample tank pressure measurements.

ANALYTICAL MODIFICATIONS

The reuse of the sample tank as the intermediate collection vessel during condensate recovery and conditioning would eliminate the necessity of measuring tank volumes and the associated error. This action is possible because the intermediate collection vessel volume (V_v) and the sample tank volume (V_s) cancel out in the calculation of condensible organic concentrations (C_c) if these volumes are equal (see Appendix D) for Method 25 equation derivations. Before the sample tank is reused, it should be flushed adequately with clean air to remove any remaining CO_2.

The Federal Register (Appendix A) procedure specifies that, during recovery of the condensate trap sample, the dry ice must be removed from the trap before switching the carrier gas flow through the trap. This method can create problems such as clogged rotameters and sample loss because the trap gases begin to expand when the dry ice is removed. If the

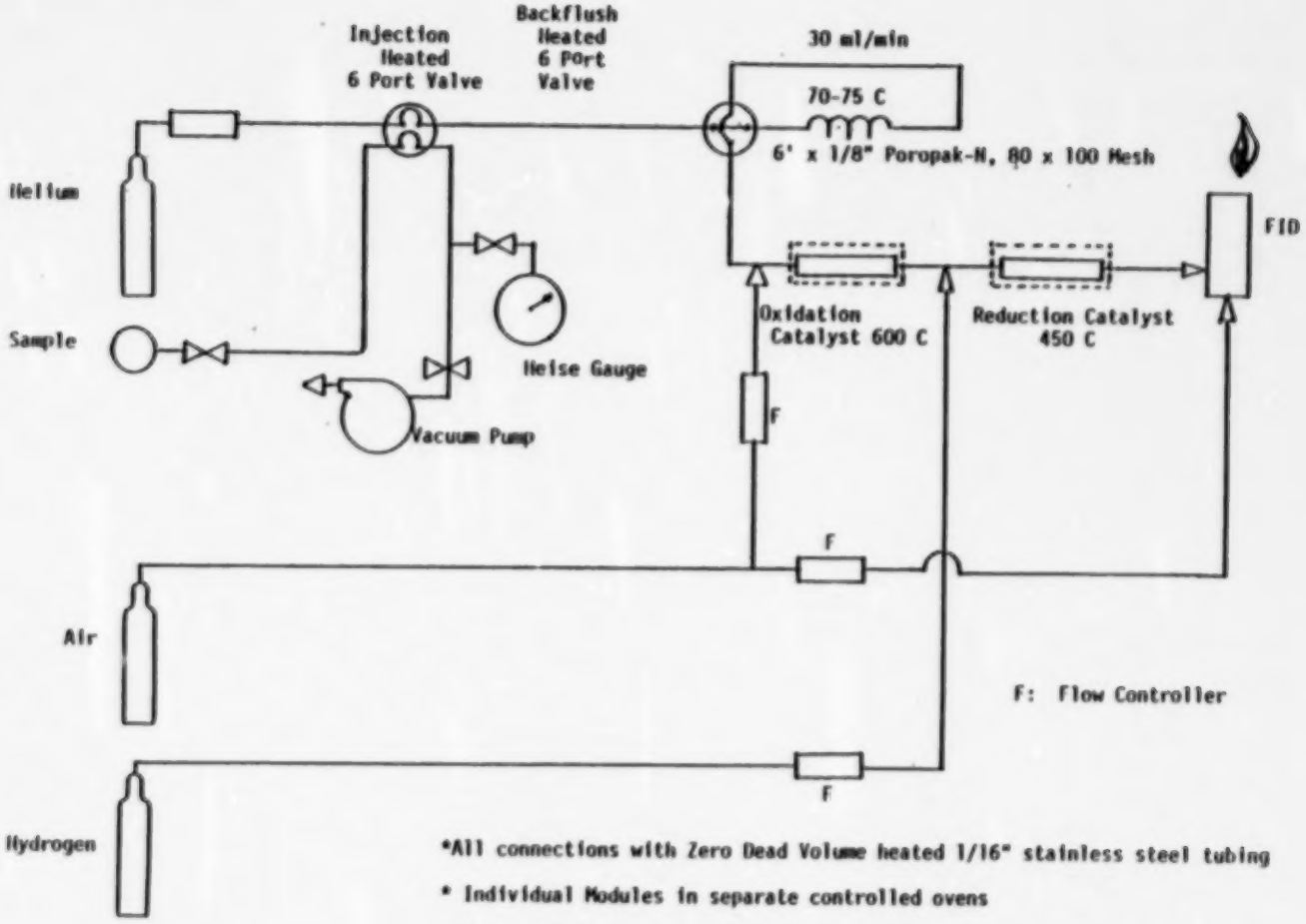

Figure 8. Improved NMO analyzer.

carrier gas is switched into this pressurized trap, water vapor or organics could expand back into the rotameters. Therefore, the carrier gas should be passed through the condensate trap before the dry ice is removed.

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APPENDIX A

EPA REFERENCE METHOD 25

3.2 Water Content. For waterborne (water reducible) coatings only, determine the weight fraction of water (W_w) using either "Standard Method of Test for Water in Water Reducible Paint by Direct Injection into a Gas Chromatograph" or "Provisional Method of Test for Water in Paint or Related Coatings by the Karl Fischer Titration Method." A waterborne coating is any coating which contains more than 5 percent water by weight in its volatile fraction. Run duplicate sets of determinations until the criterion in section 4.3 is met. Record the arithmetic average (W_w).

3.3 Coating Density. Determine the density (D_c, kg/liter) of the surface coating using the procedure in ASTM D 1475–60.

Run duplicate sets of determinations for each coating until the criterion in section 4.3 is met. Record the arithmetic average (D_c).

3.4 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

4. Data Validation Procedure

4.1 Summary. The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. This is done by running duplicate analyses on each sample tested and comparing results with the within-laboratory precision statements for each parameter. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent water increases, measured parameters for waterborne coatings are modified by the appropriate confidence limits based on between-laboratory precision statements.

4.2 Analytical Precision Statements. The within-laboratory and between-laboratory precision statements are given below:

	Within-laboratory	Between-laboratory
Volatile matter content, W_m	1.5 pct W_m	4.7 pct W_m
Water content, W_w	2.9 pct W_w	7.5 pct W_w
Density, D_c	0.001 kg/liter	0.002 kg/liter

4.3 Sample Analysis Criteria. For W_w and W_m, run duplicate analyses until the difference between the two values in a set is less than or equal to the within-laboratory precision statement for that parameter. For D_c, run duplicate analyses until each value in a set deviates from the mean of the set by no more than the within-laboratory precision statement. If after several attempts it is concluded that the ASTM procedures cannot be used for the specific coating with the established within-laboratory precision, the Administrator will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emission Standards and Engineering Division, (MD–13) Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

4.4 Confidence Limit Calculations for Waterborne Coatings. Based on the between-laboratory precision statements, calculate the confidence limits for waterborne coatings as follows:

To calculate the lower confidence limit, subtract the appropriate between-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropriate between-laboratory precision value to the measured mean value for that parameter. For W_w and D_c, use the lower confidence limits, and for W_m, use the upper confidence limit. Because V_s is calculated, there is no adjustment for the parameter.

5. Calculations

5.1 Nonaqueous Volatile Matter.

5.1.1 Solvent-borne Coatings.

$$W_s = W_m \qquad \text{Eq. 24–2}$$

Where:

W_s = Weight fraction nonaqueous volatile matter, g/g.

5.1.2 Waterborne Coatings.

$$W_s = W_m - W_w \qquad \text{Eq. 24–3}$$

5.2 Weight fraction solids.

$$W_s = 1 - W_w \qquad \text{Eq. 24–4}$$

Where: W_s = Weight solids, g/g.

6. Bibliography

6.1 Provisional Method Test for Volatile Content of Paints. Available from: Chairman, Committee D–1 on Paint and Related Coatings and Materials, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103. ASTM Designation D 2369–81.

6.2 Standard Method of Test for Density of Paint, Varnish, Lacquer, and Related Products. In: 1980 Book of ASTM Standards, Part 27. Philadelphia, Pennsylvania. ASTM Designation D 1475–60. 1980.

6.3 Standard Method of Test for Water in Water Reducible Paint by Direct Injection into a Gas Chromatograph. Available from: Chairman, Committee D–1 on Paint and Related Coatings and Materials, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103. ASTM Designation D 3792–79.

6.4 Provisional Method of Test Water in Paint or Related Coatings by the Karl Fischer Titration Method. Available from: Chairman, Committee D–1 on Paint and Related Coatings and Materials, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.

Method 25—Determination of Total Gaseous Nonmethane Organic Emissions as Carbon

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of volatile organic compounds (VOC) as total gaseous nonmethane organics (TGNMO) as carbon in source emissions. Organic particulate matter will interfere with the analysis and therefore, in some cases, an in-stack particulate filter is required. This method is not the only method that applies to the measurement of TGNMO. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular weight of the organics in the effluent stream, a totally automated semi-continuous nonmethane organic (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semi-continuously over an extended time period.

Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane will, of course, also be measured. In practice, the FID can be applied to the determination of the mass concentration of the total molecular structure of the organic emissions under the following limited conditions: (1) Where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentage of the compounds is known or can be determined, and the FID response to the compounds is known; (4) where a consistent mixture of compounds exists before and after emission control and *only* the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

1.2 Principle. An emission sample is withdrawn from the stack at a constant rate through a chilled condensate trap by means of an evacuated sample tank. TGNMO are determined by combining the analytical results obtained from independent analyses of the condensate trap and sample tank fractions. After sampling is completed, the organic contents of the condensate trap are oxidized to carbon dioxide (CO_2) which is quantitatively collected in an evacuated vessel; then a portion of the CO_2 is reduced to methane (CH_4) and measured by a FID. The organic content of the sample fraction collected in the sampling tank is measured by injecting a portion into a gas chromatographic (GC) column to achieve separation of the nonmethane organics from carbon monoxide (CO), CO_2, and CH_4; the nonmethane organics (NMO) are oxidized to

CO_2, reduced to CH_4, and measured by a FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

2. Apparatus

The sampling system consists of a condensate trap, flow control system, and sample tank (Figure 1). The analytical system consists of two major sub-systems: an oxidation system for the recovery and conditioning of the condensate trap contents and a NMO analyzer. The NMO analyzer is a GC with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. (Figures 2 and 3 are schematics of a typical NMO analyzer.) The system for the recovery and conditioning of the organics captured in the condensate trap consists of a heat source, oxidation catalyst, nondispersive infrared (NDIR) analyzer and an intermediate collection vessel (Figure 4 is a schematic of a typical system.) TGNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. NMO analyzers are available commercially or can be constructed from available components by a qualified instrument laboratory.

2.1 Sampling. The following equipment is required:

2.1.1 Probe. 3.3-mm OD (⅛-in.) stainless steel tubing.

2.1.2 Condensate Trap. Constructed of 316 stainless steel; construction details of a suitable trap are shown in Figure 5.

2.1.3 Flow Shut-off Valve. Stainless steel control valve for starting and stopping sample flow.

2.1.4 Flow Control System. Any system capable of maintaining the sampling rate to within ±10 percent of the selected flow rate (50 to 150 cc/min range).

2.1.5 Vacuum Gauge. Gauge for monitoring the vacuum of the sample tank during leak checks and sampling.

2.1.6 Sample Tank. Stainless steel or aluminum tank with a volume of 4 to 6 liters, equipped with a stainless steel female quick connect for assembly to the sample train and analytical system.

2.1.7 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1 mm Hg in the 0–900 mm range.

2.1.8 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

2.2 Analysis. The following equipment is required:

2.2.1 Condensate Recovery and Conditioning Apparatus. An apparatus for recovering and catalytically oxidizing the condensate trap contents is required. Figure 4 is a schematic of such a system. The analyst must demonstrate prior to initial use that the analytical system is capable of proper oxidation and recovery, as specified in section 5.1. The condensate recovery and conditioning apparatus consists of the following major components.

2.2.1.1 Heat Source. A heat source sufficient to heat the condensate trap (including probe) to a temperature where the trap turns a "dull red" color. A system using both a propane torch and an electric muffle-type furnace is recommended.

2.2.1.2 Oxidation Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.1.2). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.1.3 Water Trap. Any leak-proof moisture trap capable of removing moisture from the gas stream.

2.2.1.4 NDIR Detector. A detector capable of indicating CO_2 concentration in the zero to 1 percent range. This detector is required for monitoring the progress of combustion of the organic compounds from the condensate trap.

2.2.1.5 Pressure Regulator. Stainless steel needle valve required to maintain the trap conditioning system at a near constant pressure.

2.2.1.6 Intermediate Collection Vessel. Stainless steel or aluminum collection vessel equipped with a female quick connect. Tanks with nominal volumes in the 1 to 4 liter range are recommended.

2.2.1.7 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1 mm Hg in the 0–900 mm range.

2.2.1.8 Gas Purifiers. Gas purification systems sufficient to maintain CO_2 and organic impurities in the carrier gas and auxiliary oxygen at a level of less than 10 ppm (may not be required depending on quality of cylinder gases used).

2.2.2 NMO Analyzer. Semi-continuous GC/FID analyzer capable of: (1) separating CO, CO_2, and CH_4 from nonmethane organic compounds, (2) reducing the CO_2 to CH_4 and quantifying as CH_4, and (3) oxidizing the nonmethane organic compounds to CO_2, reducing the CO_2 to CH_4 and quantifying as CH_4. The analyst must demonstrate prior to initial use that the analyzer is capable of proper separation, oxidation, reduction, and measurement (section 5.2). The analyzer consists of the following major components:

2.2.2.1 Oxidation Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.2.1). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.2.2 Reduction Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.2.3). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.2.3 Separation Column(s). Gas chromatographic column(s) capable of separating CO, CO_2, and CH_4 from NMO compounds as demonstrated according to the procedures established in this method (section 5.2.5). Addendum I of this method lists a column found to be acceptable.

2.2.2.4 Sample Injection System. A GC sample injection valve fitted with a sample loop properly sized to interface with the NMO analyzer (1 cc loop recommended).

2.2.2.5 FID. A FID meeting the following specifications is required.

2.2.2.5.1 Linearity. A linear response (± 5%) over the operating range as demonstrated by the procedures established in section 5.2.2.

2.2.2.5.2 Range. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale for a full scale range of 10 to 50000 ppm CH_4.

2.2.2.6 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the analytical results.

2.2.3 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

2.2.4 Thermometer. Capable of measuring the laboratory temperature within 1°C.

2.2.5 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

2.2.6 Syringe (2). 10 µl and 100 µl liquid injection syringes.

2.2.7 Liquid Sample Injection Unit. 316 SS U-tube fitted with a Teflon injection septum, see Figure 6.

3. Reagents

3.1 Sampling. Crushed dry ice is required during sampling.

3.2 Analysis.

3.2.1 NMO Analyzer. The following gases are needed:

3.2.1.1 Carrier Gas. Zero grade gas containing less than 1 ppm C. Addendum I of this method lists a carrier gas found to be acceptable.

3.2.1.2 Fuel Gas. Pure hydrogen, containing less than 1 ppm C.

3.2.1.3 Combustion Gas. Zero grade air or oxygen as required by the detector.

3.2.2 Condensate Recovery and Conditioning Apparatus.

3.2.2.1 Carrier Gas. Five percent O_2 in N_2, containing less than 1 ppm C.

3.2.2.2 Auxiliary Oxygen. Zero grade oxygen containing less than 1 ppm C.

3.2.2.3 Hexane. ACS grade, for liquid injection.

3.2.2.4 Toluene. ACS grade, for liquid injection.

3.3 Calibration. For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder (i.e., the length of time the gas concentration is not expected to change more than ± 3 percent from its certified value). The date of gas cylinder preparation, certified organic concentration and recommended maximum shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer. The following calibration gases are required.

3.3.1 Oxidation Catalyst Efficiency Check Calibration Gas. Gas mixture standard with nominal concentration of 1 percent methane in air.

3.3.2 Flame-Ionization Detector Linearity and Nonmethane Organic Calibration Gases (3). Gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

3.3.3 Carbon Dioxide Calibration Gases (3). Gas mixture standards with nominal CO_2 concentrations of 50 ppm, 300 ppm, and 1 percent, in air. Note: total NMO less than 1 ppm required for 1 percent mixture.

3.3.4 NMO Analyzer System Check Calibration Gases (4).

3.3.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH_4, 2 percent CO_2, and 20 ppm C_3H_8, prepared in air.

3.3.4.2 Hexane. Gas mixture standard containing (nominal) 50 ppm hexane in air.

3.3.4.3 Toluene. Gas mixture standard containing (nominal) 20 ppm toluene in air.

3.3.4.4 Methanol. Gas mixture standard containing (nominal) 100 ppm methanol in air.

4. Procedure

4.1 Sampling.

4.1.1 Sample Tank Evacuation and Leak Check. Either in the laboratory or in the field, evacuate the sample tank to 10 mm Hg absolute pressure or less (measured by a mercury U-tube manometer) then leak check the sample tank by isolating the tank from the vacuum pump and allowing the tank to sit for 10 minutes. The tank is acceptable if no change in tank vacuum is noted.

4.1.2 Sample Train Assembly. Just prior to assembly, measure the tank vacuum using a mercury U-tube manometer. Record this vacuum (P_{ti}), the ambient temperature (T_a), and the barometric pressure (P_{bar}) at this time. Assuring that the flow shut-off valve is in the closed position, assemble the sampling system as shown in Figure 1. Immerse the condensate trap body in dry ice to within 2.5 or 5 cm of the point where the inlet tube joins the trap body.

4.1.3 Pretest Leak Check. A pretest leak check is required. After the sampling train is assembled, record the tank vacuum as indicated by the vacuum gauge. Wait a minimum period of 10 minutes and recheck the indicated vacuum. If the vacuum has not changed, the portion of the sampling train behind the shut-off valve does not leak and is considered acceptable. To check the front portion of the sampling train, assure that the probe tip is tightly plugged and then open the sample train flow shut-off valve. Allow the sample train to sit for a minimum period of 10 minutes. The leak check is acceptable if no visible change in the tank vacuum gauge occurs. Record the pretest leak rate (cm/Hg per 10 minutes). At the completion of the leak check period, close the sample flow shut-off valve.

4.1.4 Sample Train Operation. Place the probe into the stack such that the probe is perpendicular to the direction of stack gas flow; locate the probe tip at a single-preselected point. If a probe extension which will not be analyzed as part of the condensate trap is being used, assure that at least a 15 cm section of the probe which will be analyzed with the trap is in the stack effluent. For stacks having a negative static pressure, assure that the sample port is sufficiently sealed to prevent air in-leakage around the probe. Check the dry ice level and add ice if necessary. Record the clock time and sample tank gauge vacuum. To begin sampling, open the flow shut-off valve and adjust (if applicable) the control valve of the flow control system used in the sample train; maintain a constant flow rate (±10 percent) throughout the duration of the sampling period. Record the gauge vacuum and flowmeter setting (if applicable) at 5-minute intervals. Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulation; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained due to reduced sample tank vacuum. When the sampling is completed, close the flow shut-off valve and record the final sample time and gauge vacuum readings. Note: If the sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After removing the probe from the stack, remove the used sample tank from the sampling train (without disconnecting other portions of the sampling train) and connect another sample tank to the sampling train. Prior to attaching the new tank to the sampling train, assure that the tank vacuum (measured on-site by the U-tube manometer) has been recorded on the data form and that the tank has been leak-checked (on-site). After the new tank is attached to the sample train, proceed with the sampling until the required minimum sampling time has been exceeded.

4.1.5 Post Test Leak Check. A leak check is mandatory at the conclusion of each test run. After sampling is completed, remove the probe from the stack and plug the probe tip. Open the sample train flow shut-off valve and monitor the sample tank vacuum gauge for a period of 10 minutes. The leak check is acceptable if no visible change in the tank vacuum gauge occurs. Record the post test leak rate (cm Hg per 10 minutes). If the sampling train does not pass the post leak check, invalidate the run or use a procedure acceptable to the Administrator to adjust the data.

4.2 Sample Recovery. After the post test leak check is completed, disconnect the condensate trap at the flow metering system and tightly seal both ends of the condensate trap. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Remove the flow metering system from the sample tank. Attach the U-tube manometer to the tank (keep length of connecting line to a minimum) and record the final tank vacuum (P_{tf}); record the tank temperature (T_a) and barometric pressure at this time. Disconnect the manometer from the tank. Assure that the test run number is properly identified on the condensate trap and the sample tank(s).

4.3 Condensate Recovery and Conditioning. Prepare the condensate recovery and conditioning apparatus by setting the carrier gas flow rate and heating the catalyst to its operating temperature. Prior to initial use of the condensate recovery and conditioning apparatus, a system performance test must be conducted according to the procedures established in section 4.3 of this method. After successful completion of the initial performance test, the system is routinely used for sample conditioning according to the following procedures:

4.3.1 System Blank and Catalyst Efficiency Check. Prior to and immediately following the conditioning of each set of sample traps, or on a daily basis (whichever occurs first) conduct the carrier gas blank test and catalyst efficiency test as specified in sections 3.1.1 and 3.1.2 of this method. Record the carrier gas initial and final blank values, B_{wi} and B_{wf}, respectively. If the criteria of the tests cannot be met, make the necessary repairs to the system before proceeding.

4.3.2 Condensate Trap Carbon Dioxide Purge and Sample Tank Pressurization. The first step in analysis is to purge the condensate trap of any CO_2 which it may contain and to simultaneously pressurize the sample tank. This is accomplished as follows: Obtain both the sample tank and condensate trap from the test run to be analyzed. Set up the condensate recovery and conditioning apparatus so that the carrier flow bypasses the condensate trap hook-up terminals, bypasses the oxidation catalyst, and is vented to the atmosphere. Next, attach the condensate trap to the apparatus and pack the trap in dry ice. Assure that the valves isolating the collection vessel connection from the atmospheric vent and the vacuum pump are closed and then attach the sample tank to the system as if it were the intermediate collection vessel. Record the tank vacuum on the laboratory data form. Assure that the NDIR analyzer indicates a zero output level and then switch the carrier flow through the condensate trap; immediately switch the carrier flow from vent to collect. The condensate trap recovery and conditioning apparatus should now be set up as indicated in Figure 6. Monitor the NDIR; when CO_2 is no longer being passed through the system, switch the carrier flow so that it once again bypasses the condensate trap. Continue in this manner until the gas sample tank is pressurized to a nominal gauge pressure of 600 mm Hg. At this time, isolate the tank, vent the carrier flow, and record the sample tank pressure (P_{tf}), barometric pressure (P_{bar}), and ambient temperature (T_a). Remove the sample tank from the system.

4.3.3 Recovery of Condensate Trap Sample. Oxidation and collection of the sample in the condensate trap is now ready to begin. From the step just completed in section 4.3.1.2 above, the system should be set up so that the carrier flow bypasses the condensate trap, bypasses the oxidation catalyst, and is vented to the atmosphere. Attach an evacuated intermediate collection vessel to the system and then switch the carrier so that it flows through the oxidation catalyst. Switch the carrier from vent to collect and open the valve to the collection vessel; remove the dry ice from the trap and then switch the carrier flow through the trap. The system should now be set up to operate as indicated in Figure 6. During oxidation of the condensate trap sample, monitor the NDIR to determine when all the sample has been removed and oxidized (indicated by return to baseline of NDIR analyzer output). Begin heating the condensate trap and probe with a propane torch. The trap should be heated to a temperature at which the trap glows a "dull red" (approximately 300°C). During the early part of the trap "burn out," adjust the carrier and auxiliary oxygen flow rates so that an excess of oxygen is being fed to the catalyst system. Gradually increase the flow of carrier gas through the trap. After the NDIR indicates that most of the organic matter has been purged, place the trap in a muffle furnace (300°C). Continue to heat the probe with a torch or some other procedure (e.g., electrical resistance heater). Continue this procedure for at least 5 minutes after the NDIR has returned to baseline. Remove the heat from the trap but continue the carrier flow until the intermediate collection vessel is pressurized to a gauge pressure of 600 mm

Hg (nominal). When the vessel is pressurized, vent the carrier; measure and record the final intermediate collection vessel pressure (P_f) as well as the barometric pressure (P_{bar}), ambient temperature (T_a), and collection vessel volume (V_v).

4.4 Analysis. Prior to putting the NMO analyzer into routine operation, an initial performance test must be conducted. Start the analyzer and perform all the necessary functions in order to put the analyzer in proper working order, then conduct the performance test according to the procedures established in section 5.2. Once the performance test has been successfully completed and the CO_2 and NMO calibration response factors determined, proceed with sample analysis as follows:

4.4.1 Daily operations and calibration checks. Prior to and immediately following the analysis of each set of samples or on a daily basis (whichever occurs first) conduct a calibration test according to the procedures established in section 5.3. If the criteria of the daily calibration test cannot be met, repeat the NMO analyzer performance test (section 5.2) before proceeding.

4.4.2 Analysis of Recovered Condensate Sample. Purge the sample loop with sample and then inject a preliminary sample in order to determine the appropriate FID attenuation. Inject triplicate samples from the intermediate collection vessel and record the values obtained for the condensible organics as CO_2 (C_{con}).

4.4.3 Analysis of Sample Tank. Purge the sample loop with sample and inject a preliminary sample in order to determine the appropriate FID attenuation for monitoring the backflushed non-methane organics. Inject triplicate samples from the sample tank and record the values obtained for the nonmethane organics (C_{nm}).

5. Calibration and Operational Checks

Maintain a record of performance of each item.

5.1 Initial Performance Check of Condensate Recovery and Conditioning Apparatus.

5.1.1 Carrier Gas and Auxiliary Oxygen Blank. Set equal flow rates for both the carrier gas and auxiliary oxygen. With the trap switching valves in the bypass position and the catalyst in-line, fill an evacuated intermediate collection vessel with carrier gas. Analyze the collection vessel for CO_2; the carrier blank is acceptable if the CO_2 concentration is less than 10 ppm.

5.1.2 Catalyst Efficiency Check. Set up the condensate trap recovery system so that the carrier flow bypasses the trap inlet and is vented to the atmosphere at the system outlet. Assure that the valves isolating the collection system from the atmospheric vent and vacuum pump are closed and then attach an evacuated intermediate collection vessel to the system. Connect the methane standard gas cyclinder (section 3.3.1) to the system's condensate trap connector (probe end, Figure 4). Adjust the system valving so that the standard gas cylinder sets as the carrier gas and adjust the flow rate to the rate normally used during trap sample recovery. Switch off the auxiliary oxygen flow and then switch from vent to collect in order to begin collecting a sample. Continue collecting a sample in a normal manner until the intermediate vessel is filled to a nominal gauge pressure of 300 mm Hg. Remove the intermediate vessel from the system and vent the carrier flow to the atmosphere. Switch the valving to return the system to its normal carrier gas and normal operating conditions. Analyze the collection vessel for CO_2; the catalyst efficiency is acceptable if the CO_2 concentration is within ±5 percent of the expected value.

5.1.3 System Performance Check. Construct a liquid sample injection unit similar in design to the unit shown in Figure 6. Insert this unit into the condensate recovery and conditioning system in place of a condensate trap and set the carrier gas and auxiliary oxygen flow rates to normal operating levels. Attach an evacuated intermediate collection vessel to the system and switch from system vent to collect. With the carrier gas routed through the injection unit and the oxidation catalyst, inject a liquid sample (see. 5.1.3.1 to 5.1.3.4) via the injection septum. Heat the injection unit with a torch while monitoring the oxidation reaction on the NDIR. Continue the purge until the reaction is complete. Measure the final collection vessel pressure and then analyze the vessel to determine the CO_2 concentration. For each injection, calculate the percent recovery using the equation in section 6.6.

The performance test is acceptable if the average percent recovery is 100 ± 10 percent with a relative standard deviation (section 6.7) of less than 5 percent for each set of triplicate injections as follows:

5.1.3.1 100 µl hexane.
5.1.3.2 10 µl hexane.
5.1.3.3 100 µl toluene.
5.1.3.4 10 µl toluene.

5.2 Initial NMO Analyzer Performance Test.

5.2.1 Oxidation Catalyst Efficiency Check. Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (section 3.3.1). The oxidation catalyst operation is acceptable if no FID response is noted.

5.2.2 Analyzer Linearity Check and NMO Calibration. Operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in section 3.3, make triplicate injections of each calibration gas and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within ±5 percent of the overall mean value and if the relative standard deviation (section 6.7) for each set of triplicate injections is less than ±5 percent. Record the overall mean of the propane response factor values as the NMO calibration response factor (RF_{nmo}).

5.2.3 Reduction Catalyst Efficiency Check and CO_2 Calibration. An exact determination of the reduction catalyst efficiency is not required. Instead, proper catalyst operation is indirectly checked and continuously monitored by establishing a CO_2 response factor and comparing it to the NMO response factor. Operating both the oxidation and reduction catalysts make triplicate injections of each of the CO_2 calibration gases (section 3.3.3). Calculate the average response factor (area/ppm) for each calibration gas, as well as the overall mean of the response factor values. The reduction catalyst operation is acceptable if the average response factor of each calibration gas is within ±5 percent of the overall mean value and if the relative standard deviation (section 6.7) for each set of triplicate injections is less than ±5 percent. Additionally, the CO_2 overall mean response factor must be within ±10 percent of the NMO calibration response factor (RF_{nmo}) calculated in section 5.2.2. Record the overall mean of the response factor values as the CO_2 calibration response factor (RF_{co_2}).

5.2.4 NMO System Blank. For the high level CO_2 calibration gas (section 3.3.3) record the NMO value measured during the CO_2 calibration conducted in section 5.2.3. This value is the NMO blank value for the analyzer (B_a) and should be less than 10 ppm.

5.2.5 System Performance Check. Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in section 3.3.4. The analyzer performance is acceptable if the measured NMO value for each gas (average of triplicate injections) is within ±12 percent of the expected value.

5.3 NMO Analyzer Daily Calibration.

5.3.1 NMO Blank and CO_2. Inject triplicate samples of the high level CO_2 calibration gas (section 3.3.3) and calculate the average response factor. The system operation is adequate if the calculated response factor is within ±10 percent of the RF_{nmo} calculated during the initial performance test (section 5.2.2). Use the daily response factor (DRF_{nmo}) for analyzer calibration and the calculation of measured CO_2 concentrations in the collection vessel samples. In addition, record the NMO blank value (B_a); this value should be less than 10 ppm.

5.3.2 NMO Calibration. Inject triplicate samples of the mixed propane calibration cylinder (section 3.3.4.1) and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within ±10 percent of the RF_{nmo} calculated during the initial performance test (section 5.2.1). Use the daily response factor (DRF_{nmo}) for analyzer calibration and calculation of NMO concentrations in the sample tanks.

5.4 Sample Tank. The volume of the gas sampling tanks used must be determined. Prior to putting each tank in service, determine the tank volume by weighing the tanks empty and then filled with deionized distilled water; weigh to the nearest 5 gm and record the results. Alternatively, measure the volume of water used to fill the tanks to the nearest 5 ml.

5.5 Intermediate Collection Vessel. The volume of the intermediate collection vessels used to collect CO_2 during the analysis of the condensate traps must be determined. Prior to putting each vessel into service, determine the volume by weighing the vessel empty and then filled with deionized distilled water; weigh to the nearest 5 gm and record the results. Alternatively, measure the volume of water used to fill the tanks to the nearest 5 ml.

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6. Calculations

Note: All equations are written using absolute pressures; absolute pressures are determined by adding the measured barometric pressure to the measured gauge pressure.

6.1 Sample Volume. For each test run, calculate the gas volume sampled:

$$V_s = 0.386\ V \left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}} \right)$$

6.2 Noncondensible Organics. For each sample tank, determine the concentration of nonmethane organics (ppm C):

$$C_t = \left[\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \right] \left[\frac{1}{F} \sum_{j=1}^{F} C_{cm_j} - B_a \right]$$

6.3 Condensible Organics. For each condensate trap determine the concentration of organics (ppm C):

$$C_c = 0.386 \frac{V_y}{V_s} \frac{P_f}{T_f} \left[\frac{1}{q} \sum_{k=1}^{q} C_{cm_k} - B_t \right]$$

6.4 Total Gaseous Nonmethane Organics (TGNMO). To determine the TGNMO concentration for each test run, use the following equation:

$$C = C_t + C_c$$

6.5 Total Gaseous Nonmethane Organics (TGNMO) Mass Concentration. To determine the TGNMO mass concentration as carbon for each test run, use the following equation:

$$M_C = 0.498\ C$$

6.6 Percent Recovery. To calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system use the following equation:

$$\text{percent recovery} = 1.6 \frac{M}{L} \frac{V_y}{\rho} \frac{P_f}{T_f} \frac{C_{cm}}{R}$$

6.7 Relative Standard Deviation.

$$RSD = \frac{100}{\bar{x}} \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}}$$

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Where:

R_a = Measured NMO blank value for NMO analyzer, ppm C.

R_b = Measured CO_2 [illegible] CO_2.

C = total gaseous nonmethane organic (TGNMO) concentration of the effluent, ppm C equivalent.

C_c = Calculated condensible organic (condensate trap) concentration of the effluent, ppm C equivalent.

C_{cm} = Measured concentration (NMO analyzer) for the condensate trap (intermediate collection vessel), ppm CO_2.

C_n = Calculated noncondensible organic concentration (sample tank) of the effluent, ppm C equivalent.

C_{nm} = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.

L = Volume of liquid injected, microliters.

M = Molecular weight of the liquid injected, g/g-mole.

M_t = total gaseous non-methane organic (TGNMO) mass concentration of the effluent, mg C/dscm.

N = Carbon number of the liquid compound injected (N = 7 for toluene, N = 6 for hexane).

P_f = Final pressure of the intermediate collection vessel, mm Hg absolute.

P_o = Gas sample tank pressure prior to sampling, mm Hg absolute.

P_i = Gas sample tank pressure after sampling, but prior to pressurizing, mm Hg absolute.

P_p = Final gas sample tank pressure after pressurizing, mm Hg absolute.

T_f = Final temperature of intermediate collection vessel, °K.

T_o = Sample tank temperature prior to sampling, °K.

T_i = Sample tank temperature at completion of sampling, °K.

T_p = Sample tank temperature after pressurizing °K.

V = Sample tank volume, cm.

V_f = Intermediate collection vessel volume, cm.

V_s = Gas volume sampled, dscm.

n = Number of data points.

q = Total number of analyzer injections of intermediate collection vessel during analysis (where k = injection number, 1 . . . q).

r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 . . . r).

x_i = individual measurements.

X = Mean value.

ρ = Density of liquid injected, g/cc.

7. Bibliography

7.1 Sale, Albert E., Samuel Witz, and Robert D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 73-33.2 (Presented at the 66th Annual Meeting of the Air Pollution Control Association, Boston, MA, June 15-20, 1973.) 14 p.

7.2 Sale, Albert E., William L. Oaks, and Robert D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74-180. (Presented at the 67th Annual Meeting of the Air Pollution Control Association, Denver, CO, June 9-13, 1974.) 23 p.

Method 25

Addendum 1. System Components

In test Method 25 several important system components are not specified; instead minimum performance specifications are provided. The method is written in this manner to permit individual preference in choosing components, as well as to encourage development and use of improved components. This addendum is added to the method in order to provide users with some specific information regarding components which have been found satisfactory for use with the method. This listing is given only for the purpose of providing information and does not constitute an endorsement of any product by the Environmental Protection Agency. This list is not meant to imply that other components not listed are not acceptable.

1. Condensate Recovery and Conditioning System Oxidation Catalyst. ⅜" OD×14" Inconel tubing packed with 8 inches of hopcalite* oxidizing catalyst and operated at 800°C in a tube furnace. Note: At this temperature, this catalyst must be purged with carrier gas at all times to prevent catalyst damage.

2. NMO Analyzer Oxidation Catalyst. ¼" OD×14" inconel tubing packed with 6 inches of hopcalite oxidizing catalyst and operated at 800°C in a tube furnace. (See note above.)

3. NMO Analyzer Reduction Catalyst. Reduction Catalyst Module: Byron Instruments, Raleigh, N.C.

4. Gas Chromatographic Separation Column. ⅛ inch OD stainless steel packed with 3 feet of 10 percent methyl silicone, Bp 2100 (or equivalent) on Supelcoport (or equivalent), 80/100 mesh, followed by 1.5 feet Porapak Q (or equivalent) 80/80 mesh. The inlet side is to the silicone. Condition the column for 24 hours at 220°C with 30 cc/min N_2 purge.

During analysis for the nonmethane organics the separation column is operated as follows: First, operate the column at −78°C (dry ice bath) to elute CO and CH_4. After the CH_4 peak operate the column at 0°C to elute CO_2. When the CO_2 is completely eluted, switch the carrier flow to backflush the column and simultaneously raise the column temperature to 100°C in order to elute all nonmethane organics (exact timings for column operation are determined from the calibration standard).

Note.—The dry ice operating condition may be deleted if separation of CO and CH_4 is unimportant.

Note.—Ethane and ethylene may or may not be measured using this column: whether or not ethane and ethylene are quantified will depend on the CO_2 concentration in the gas sample. When high levels of CO_2 are present, ethane and ethylene will elute under the tail of the CO_2 peak.

5. Carrier Gas. Zero grade nitrogen or helium or zero air.

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*Hopcalite registered trademark.

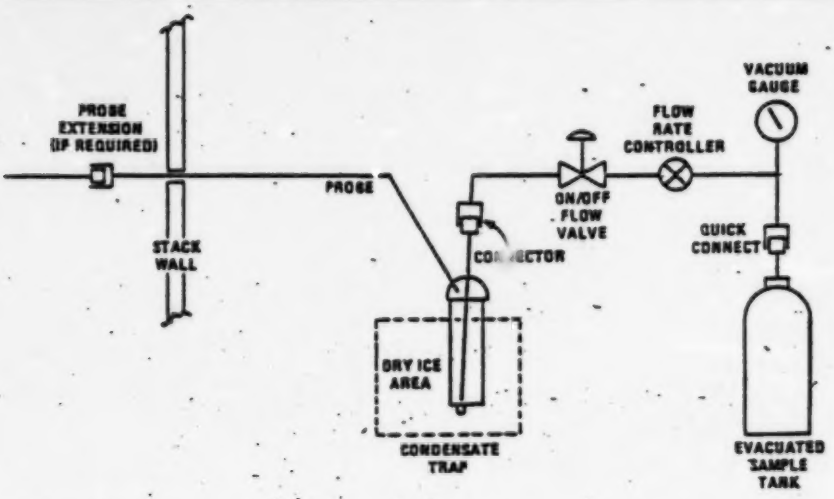

Figure 1. Sampling apparatus.

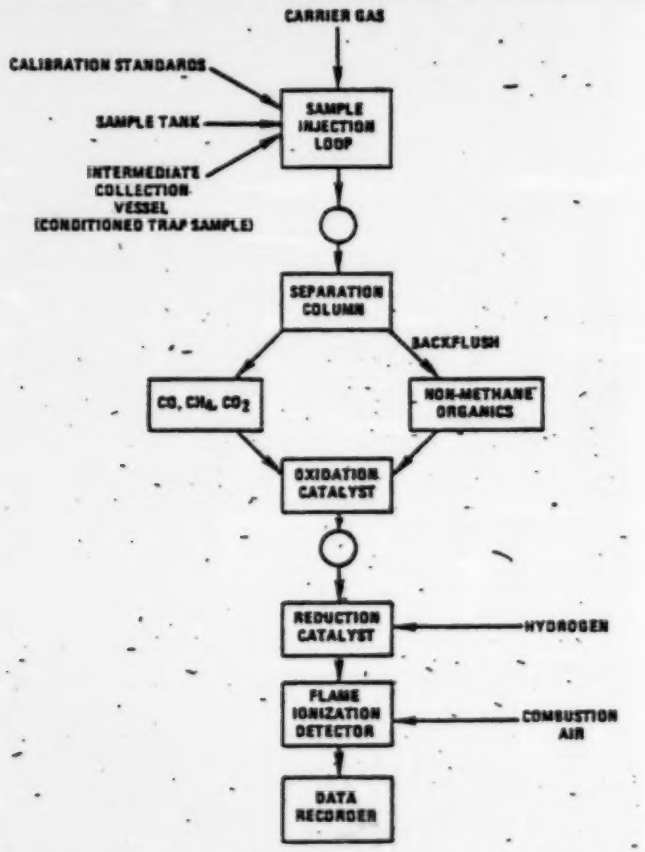

Figure 2. Simplified schematic of non-methane organic (NMO) analyzer.

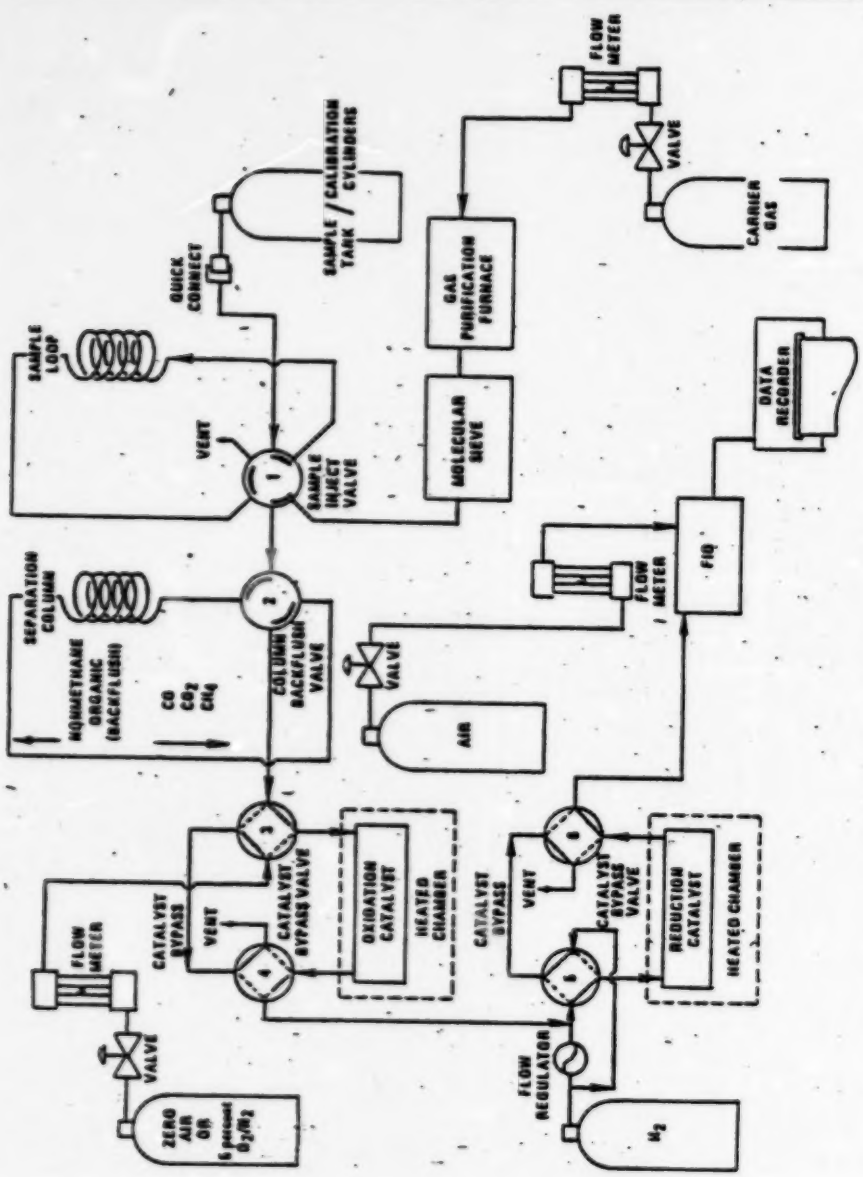

Figure 3. Nonmethane organic (NMO) analyzer.

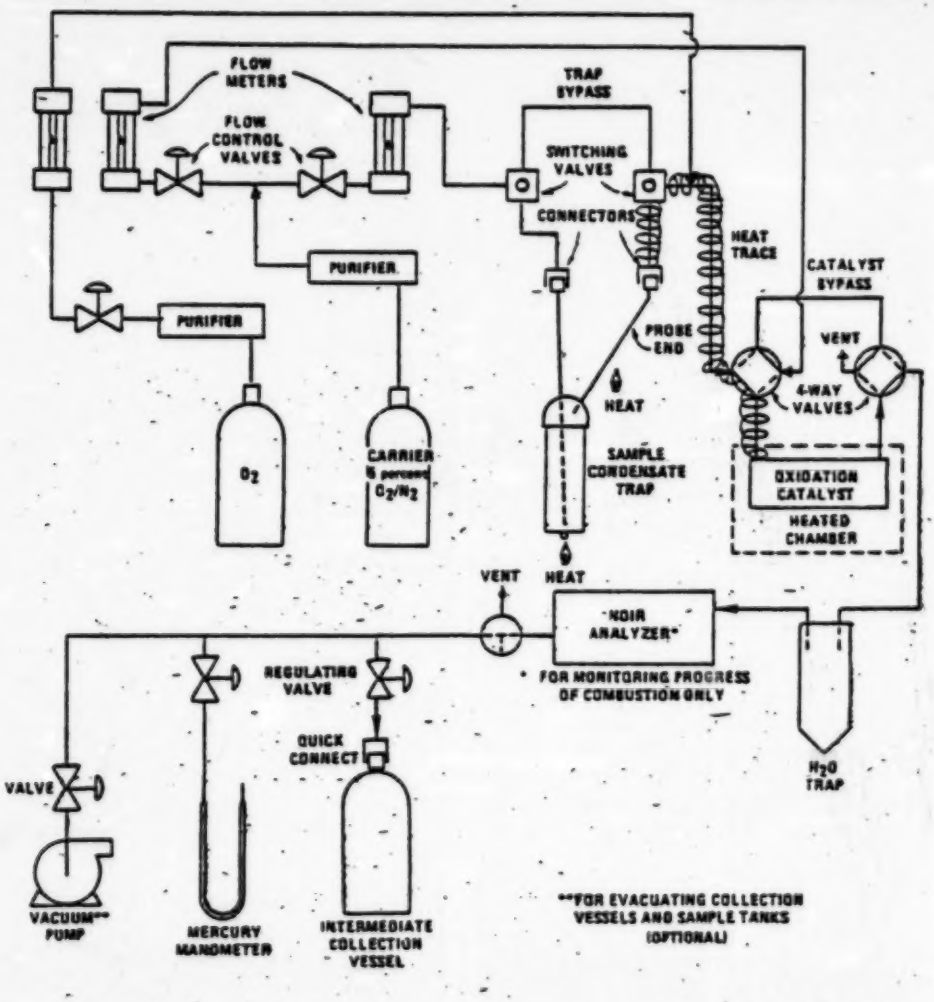

Figure 4. Condensate recovery and conditioning apparatus.

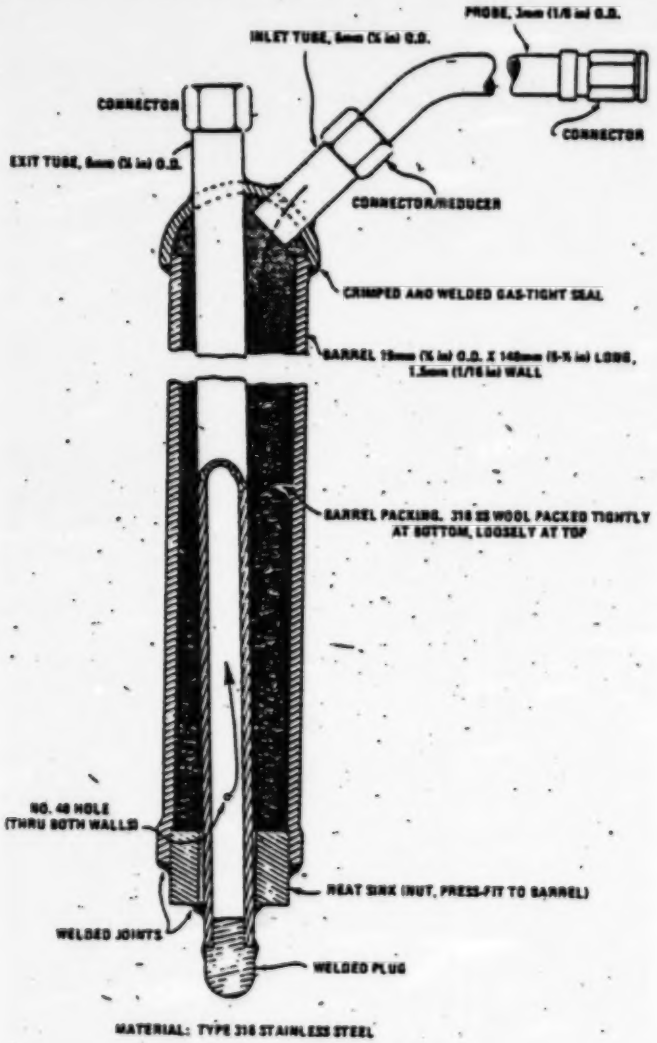
PROBE, 3mm (1/8 in) O.D.
INLET TUBE, 6mm (¼ in) O.D.
CONNECTOR
CONNECTOR
EXIT TUBE, 6mm (¼ in) O.D.
CONNECTOR/REDUCER
CRIMPED AND WELDED GAS-TIGHT SEAL
BARREL 19mm (¾ in) O.D. X 140mm (5-½ in) LONG, 1.5mm (1/16 in) WALL
BARREL PACKING, 316 SS WOOL PACKED TIGHTLY AT BOTTOM, LOOSELY AT TOP
NO. 48 HOLE (THRU BOTH WALLS)
HEAT SINK (NUT, PRESS-FIT TO BARREL)
WELDED JOINTS
WELDED PLUG
MATERIAL: TYPE 316 STAINLESS STEEL

Figure 5. Condensate trap[2].

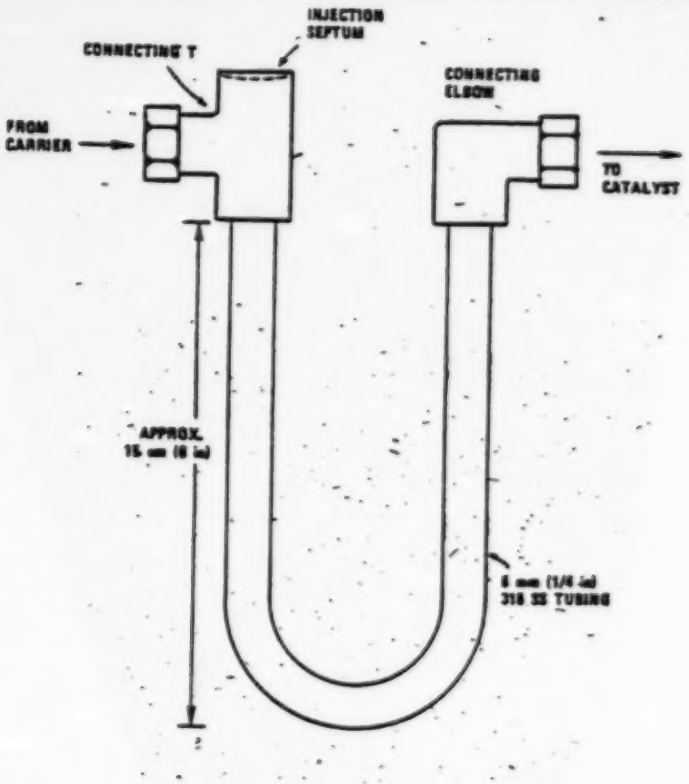

Figure 6. Liquid sample injection unit.

VOLATILE ORGANIC CARBON

FACILITY _____ SAMPLE LOCATION _____

LOCATION _____ OPERATOR _____

DATE _____ RUN NUMBER _____

TANK NUMBER _____ TRAP NUMBER _____ SAMPLE ID NUMBER _____

	TANK VACUUM, mm Hg	cm Hg	BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)		(GAUGE)		
POST TEST (MANOMETER)		(GAUGE)		

LEAK RATE _____ cm Hg / 10 min

PRETEST _____

POST TEST _____

TIME CLOCK/SAMPLE	GAUGE VACUUM, cm Hg	FLOWMETER SETTING	COMMENTS

Figure 7. Example Field Data Form.

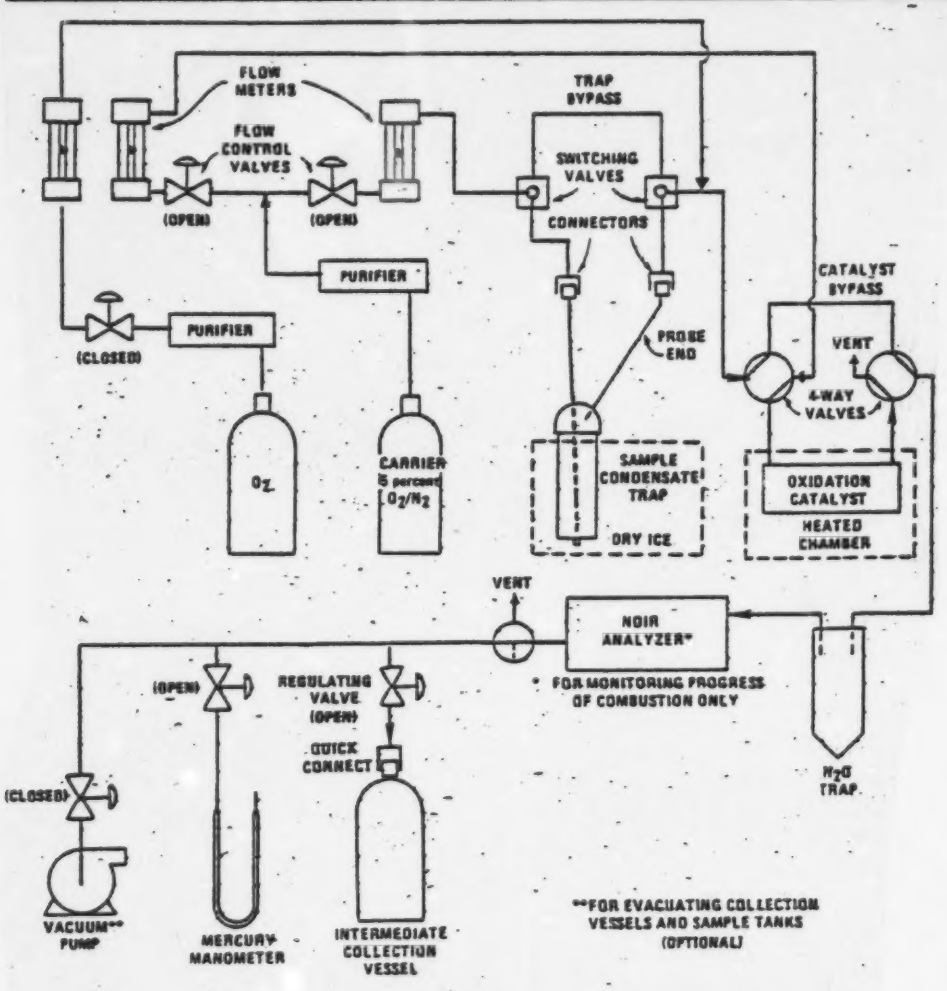

Figure 8. Condensate recovery and conditioning apparatus, carbon dioxide purge.

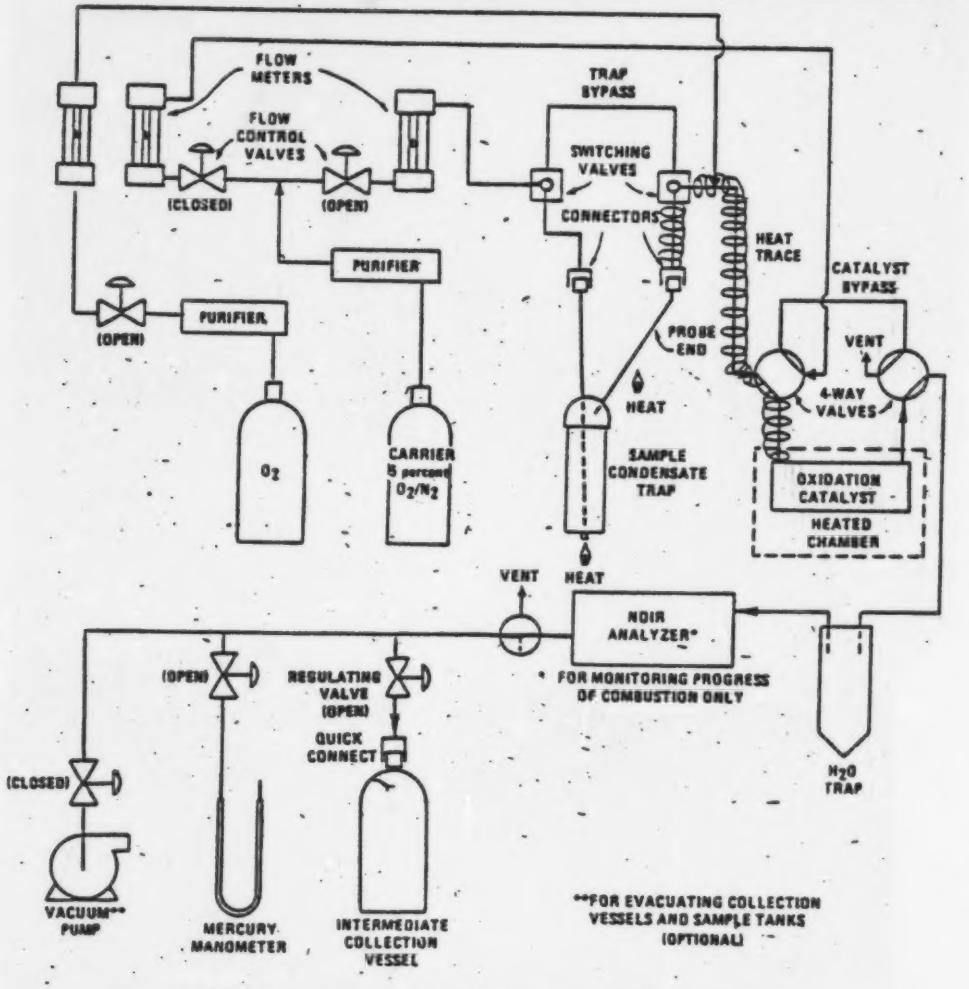

Figure 9. Condensate recovery and conditioning apparatus, collection of trap organics.

[FR Doc. 80-30758 Filed 10-2-80; 8:45 am]
BILLING CODE 6560-01-C

APPENDIX B

FIELD SAMPLING DATA SHEETS

VOLATILE ORGANIC CARBON

FACILITY Texfi Int. SAMPLE LOCATION Cloth Frame dryer exhaust
LOCATION Kinston N.C. OPERATOR Howe
DATE 5-20-91 RUN NUMBER 3-Train B
TANK NUMBER A-36 TRAP NUMBER A-4 SAMPLE ID NUMBER Low flow device

	TANK VACUUM, mm Hg	mm Hg	BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)	-752	(GAUGE) >760	29.94"	15.3
POST TEST (MANOMETER)	-306	(GAUGE) 370	29.94"	15.3

LEAK RATE mm Hg / 10 min
PRETEST <1
POST TEST <1

TIME CLOCK/SAMPLE	GAUGE VACUUM, mm Hg	FLOWMETER SETTING	COMMENTS
0 (43:22)	>760		
5	670		
10	570		
15	470		
20	370		
	—		

Sampling rate = 54 cc/min

VOLATILE ORGANIC CARBON

FACILITY Texfi Ind. SAMPLE LOCATION Cloth frame dryer exhaust
LOCATION Kinston, N.C. OPERATOR Ganaway
DATE 5-20-91 RUN NUMBER 1-Train A
TANK NUMBER A-31 TRAP NUMBER B-1 SAMPLE ID NUMBER Lo flow dry ice

	TANK VACUUM, mm Hg		BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)	753 (GAUGE)	>760	29.8"	15.7
POST TEST (MANOMETER)	311 (GAUGE)	39.0	29.9"	14.1

LEAK RATE mm Hg / 10 min
PRETEST <1
POST TEST <1

TIME CLOCK/SAMPLE	GAUGE VACUUM, mm Hg	FLOWMETER SETTING	COMMENTS
0 (9:54)	>760		
5	700		
10	640		
15	570		
20	510		
25	450		
30	390		

Sampling rate = 35 cc/min

VOLATILE ORGANIC CARBON

FACILITY Texfi Ind. SAMPLE LOCATION Cloth frame dryer exhaust
LOCATION Kinston, N.C. OPERATOR Encotech
DATE 5-20-91 RUN NUMBER 3-Train A
TANK NUMBER A-38 TRAP NUMBER B-3 SAMPLE ID NUMBER High flow, dry run

	TANK VACUUM, mm Hg		BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)	753	(GAUGE) >710	29.94"	15
POST TEST (MANOMETER)	-265	(GAUGE) 360	29.94"	15

LEAK RATE mm Hg / 10 min
PRETEST <1
POST TEST <1

TIME CLOCK/SAMPLE	GAUGE VACUUM, mm Hg	FLOWMETER SETTING	COMMENTS
0	790		
5	668		
10	560		
15	458		
20	360		
Final	340		
Final	332		
			After leak check, down to 310 (possible leak).
	—		Valve on cam was closed.

Sampling rate = 54 cc/min

VOLATILE ORGANIC CARBON

FACILITY Texfi Inc. SAMPLE LOCATION Cloth frame dryer exhaust
LOCATION Kinston N.C OPERATOR Howe
DATE 5-20-81 RUN NUMBER 1-Train B
TANK NUMBER A-211 TRAP NUMBER A-1 SAMPLE ID NUMBER Low flow dry ice

	TANK VACUUM, mm Hg		BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)	-753 (GAUGE)	>76	29.80	15.7
POST TEST (MANOMETER)	-756 (GAUGE)	32.5	29.90	14.1

LEAK RATE mm Hg / 10 min
PRETEST <1
POST TEST <1

TIME CLOCK/SAMPLE	GAUGE VACUUM, mm Hg	FLOWMETER SETTING	COMMENTS
0 (10:00)	>760		Needle valve not
5	760		open properly -
10	625		flow not matched
15	580		with train A during
20	495		first 5 minutes
25	400		
30	325		

Sampling rate = 51 cc/min

VOLATILE ORGANIC CARBON

FACILITY Teafi Incl — SAMPLE LOCATION Cloth Frame Dryer exhaust
LOCATION Kinston N.C. — OPERATOR Ganawal
DATE 5-24-91 — RUN NUMBER 4 - Train A
TANK NUMBER A-91 — TRAP NUMBER R-4 — SAMPLE ID NUMBER Low flow ISS w.t.

	TANK VACUUM, mm Hg		mm Hg	BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)	-253	(GAUGE)	>76	29.96"	14.6
POST TEST (MANOMETER)	-358	(GAUGE)	43.0	29.96"	14.6

LEAK RATE — mm Hg / 10 min
PRETEST <1
POST TEST <1

TIME CLOCK/SAMPLE	GAUGE VACUUM, mm Hg	FLOWMETER SETTING	COMMENTS
0	790		
5	700		
10	602		
15	500		
20	430		
	—		

. Sampling rate = 46cc/min

VOLATILE ORGANIC CARBON

FACILITY Texti Ind. SAMPLE LOCATION Cloth frame dryer exhaust
LOCATION Kinston N.C. OPERATOR HCL
DATE 5-20-81 RUN NUMBER 2 - Train B
TANK NUMBER A-109 TRAP NUMBER A-3 SAMPLE ID NUMBER Low flow, dry ice

	TANK VACUUM, mm Hg		mm Hg	BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)	-748	(GAUGE)	>76	29.92	14.5
POST TEST (MANOMETER)	-284	(GAUGE)	37.5	29.92	14.5

LEAK RATE mm Hg / 10 min
PRETEST <1
POST TEST <1

TIME CLOCK/SAMPLE	GAUGE VACUUM, mm Hg	FLOWMETER SETTING	COMMENTS
0 (11:30)	755		
5	655		
10	555		
15	465		
20	375		

Sampling rate: 48cc/min

VOLATILE ORGANIC CARBON

FACILITY Teefi Ind. SAMPLE LOCATION Cloth Frame Dryer exhaust
LOCATION Kingston, N.S. OPERATOR Hans
DATE 5-20-81 RUN NUMBER 4-Train B
TANK NUMBER A-44 TRAP NUMBER A-2 SAMPLE ID NUMBER Low flow dry ice

	TANK VACUUM, mm Hg		mm Hg	BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)	-753	(GAUGE)	>760	29.96	14.6
POST TEST (MANOMETER)	-338	(GAUGE)	760	29.96	14.6

LEAK RATE mm Hg / 10 min
PRETEST <1
POST TEST <1

TIME CLOCK/SAMPLE	GAUGE VACUUM, mm Hg	FLOWMETER SETTING	COMMENTS
0 (14:37)	>760		
5	680		
10	595		
15	490		
20	400		
	—		

Sampling rate = 50cc/min

VOLATILE ORGANIC CARBON

FACILITY Texti Ind. SAMPLE LOCATION Cloth frame dryer exhaust
LOCATION Kinston N.C. OPERATOR Grunewal
DATE 5-20-81 RUN NUMBER 2-Train A
TANK NUMBER A-6 TRAP NUMBER B-2 SAMPLE ID NUMBER Low flow dry ice

	TANK VACUUM, mm Hg		mm Hg	BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)	-751	(GAUGE)	>736	29.92	14.5
POST TEST (MANOMETER)	-382	(GAUGE)	46.0	29.92	14.5

LEAK RATE mm Hg / 10 min
PRETEST <1
POST TEST <1

TIME CLOCK/SAMPLE	GAUGE VACUUM, mm Hg	FLOWMETER SETTING	COMMENTS
0 (11:30)	790		
5	710		
10	632		
16	542		
20	490		
Final	475		
Final	460		

Sampling rate = 3 ℓ/min

VOLATILE ORGANIC CARBON

FACILITY Weyerhaeuser Co. SAMPLE LOCATION Veneer dryer exhaust
LOCATION Jacksonville, N.C. OPERATOR Gangmel
DATE 9-9-81 RUN NUMBER 1
TANK NUMBER A-36 TRAP NUMBER A2,07 SAMPLE ID NUMBER 1A

	TANK VACUUM, mm Hg		mm Hg	BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (BAROMETER)	-755	(GAUGE)	>76.0	29.88"	25.0
POST TEST (BAROMETER)	-494	(GAUGE)	60.0	755.7	24.5

LEAK RATE mm Hg / 10 min
PRETEST <1
POST TEST <1

TIME CLOCK/SAMPLE	GAUGE VACUUM, mm Hg	FLOWMETER SETTING	COMMENTS
0	>76.0	79	25cc/min sampling rate
5	>76.0	79	
10	71.0	79	
15	65.5	79	Both leak checks performed.
20	66.0	79	

VOLATILE ORGANIC CARBON

FACILITY Weyerhaeuser Co. SAMPLE LOCATION Veneer dryer exhaust
LOCATION Jacksonville, N.C. OPERATOR Howe
DATE 9-9-81 RUN NUMBER 1
TANK NUMBER A-31 TRAP NUMBER B-4 CP SAMPLE ID NUMBER 1B

	TANK VACUUM, mm Hg		GAUGE, mm Hg	BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)	-756	(GAUGE)	>76.0	29.88"	25.0
POST TEST (MANOMETER)	-487	(GAUGE)	57.0	755.?	24.5

LEAK RATE mm Hg / 10 min
PRETEST <1
POST TEST <1

TIME CLOCK/SAMPLE	GAUGE VACUUM, mm Hg	FLOWMETER SETTING	COMMENTS
0	>76.0	78	25 cc/min sampling
5	73.0	78	rate
10	68.0	78	
15	63.0	78	Leak corrected
20	57.0	78	during pretest
			leak check
			Stack temp = 300°F
			Both leak checks
			performed

VOLATILE ORGANIC CARBON

FACILITY Weyerhauser Co. SAMPLE LOCATION Veneer dryer exhaust
LOCATION Jacksonville, N.C. OPERATOR Gangwal
DATE 9-9-91 RUN NUMBER 2
TANK NUMBER A-39 TRAP NUMBER A-5.04 SAMPLE ID NUMBER 2A

	TANK VACUUM, mm Hg		BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)	-756. (GAUGE)	>76.0	29.88"	24.5
POST TEST (MANOMETER)	-488 (GAUGE)	59.5	755.7	24.5

LEAK RATE mm Hg / 10 min
PRETEST <1
POST TEST <1

TIME CLOCK/SAMPLE	GAUGE VACUUM, mm Hg	FLOWMETER SETTING	COMMENTS
0	>76.0	78	25cc/min. Sampling
5	76.0	78	rate
10	70.5	78	
15	65.0	78	Both leak checks
20	59.5	78	performed

VOLATILE ORGANIC CARBON

FACILITY Weyerhaeuser Co. SAMPLE LOCATION Veneer dryer exhaust
LOCATION Jacksonville, N.C. OPERATOR Howe
DATE 9-9-91 RUN NUMBER 2
TANK NUMBER A-211 TRAP NUMBER A-4 O/B SAMPLE ID NUMBER 2B

	TANK VACUUM, mm Hg		mm Hg	BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)	-756	(GAUGE)	>760	759.8	25.0
POST TEST (MANOMETER)	-494	(GAUGE)	58.0	755.7	24.5

LEAK RATE mm Hg / 10 min
PRETEST <1
POST TEST <1

TIME CLOCK/SAMPLE	GAUGE VACUUM, mm Hg	FLOWMETER SETTING	COMMENTS
0	>760	78	75cc/min. sampling
5	730	78	rate
10	680	78	
15	630	78	Stack temp = 290°F
20	580	78	
			Both leak checks
			performed

VOLATILE ORGANIC CARBON

FACILITY Weyerhaeuser Co. SAMPLE LOCATION Veneer dryer exhaust
LOCATION Jacksonville, N.C. OPERATOR Jaycaty
DATE 9-9-81 RUN NUMBER 3
TANK NUMBER A-39 TRAP NUMBER A-3.11 SAMPLE ID NUMBER 3A

	TANK VACUUM, mm Hg		mm Hg	BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)	-754	(GAUGE)	>76.0	29.88"	25.0
POST TEST (MANOMETER)	-719	(GAUGE)	48.5	755.7	24.5

LEAK RATE mm Hg / 10 min
PRETEST 21
POST TEST —

TIME CLOCK/SAMPLE	GAUGE VACUUM, mm Hg	FLOWMETER SETTING	COMMENTS
0	>76.0	78	25 cc/min. sampling
5	75.8	78	rate
10	70.2	78	
15	65.0	78	Pretest leak check
20	59.5	78	only.
25	54.0	78	
30	48.5	78	

VOLATILE ORGANIC CARBON

FACILITY Weyerhaeuser Co. SAMPLE LOCATION Veneer dryer exhaust
LOCATION Jacksonville, N.C. OPERATOR Howe
DATE 9-9-81 RUN NUMBER 3
TANK NUMBER A-91 TRAP NUMBER B-3,02 SAMPLE ID NUMBER 3B

	TANK VACUUM, mm Hg		BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)	-755	(GAUGE) >76.0	29.88"	25.0
POST TEST (MANOMETER)	-423	(GAUGE) 47.0	755.7	24.5

LEAK RATE mm Hg / 10 min
PRETEST <1
POST TEST —

TIME CLOCK/SAMPLE	GAUGE VACUUM, mm Hg	FLOWMETER SETTING	COMMENTS
0	>76.0	78	35cc/min sampling
5	73.0	78	rate
10	68.5	78	
15	63.5	78	Pretest leak check
20	58.0	78	only.
25	53.0	78	
30	47.0	78	

VOLATILE ORGANIC CARBON

FACILITY Weyerhaeuser Co. SAMPLE LOCATION Veneer dryer exhaust
LOCATION Jacksonville, N C OPERATOR Grenivial
DATE 9-9-81 RUN NUMBER V4
TANK NUMBER A-203 TRAP NUMBER A-109 SAMPLE ID NUMBER 4A

	TANK VACUUM, mm Hg		mm Hg	BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)	-756	(GAUGE)	>76.0	29.88"	25.0
POST TEST (MANOMETER)	-493	(GAUGE)	57.0	755.7	24.5

LEAK RATE mm Hg / 10 min
PRETEST 21
POST TEST —

TIME CLOCK/SAMPLE	GAUGE VACUUM, mm Hg	FLOWMETER SETTING	COMMENTS
0	>76.0	65	20 cc/min. sampling
5.3	>76.0	65	rate
10	>76.0	65	
15	72.2	65	Pretest leak check
20	107.5	65	of tank side of
25	102.1	65	needle valve.
30	57.0	65	

VOLATILE ORGANIC CARBON

FACILITY Weyerhaeuser Co. SAMPLE LOCATION Veneer dryer exhaust
LOCATION Tarboro, N.C. OPERATOR Hawe
DATE 9-9-81 RUN NUMBER 4
TANK NUMBER A-109 TRAP NUMBER B-2, C-3 SAMPLE ID NUMBER 4B

	TANK VACUUM, mm Hg		mm Hg	BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)	-756	(GAUGE)	>760.0	29.88"	25.0
POST TEST (MANOMETER)	-751	(GAUGE)	26.5	755.7	24.5

LEAK RATE mm Hg / 10 min
PRETEST <1
POST TEST —

TIME CLOCK/SAMPLE	GAUGE VACUUM, mm Hg	FLOWMETER SETTING	COMMENTS
0	>760.0	112	40 cc/min sampling
5.5	73.5	112	rate
10.1	65.5	112	
15	56.2	112	Pretest leak check
20	47.0	112	of tank side of
25	36.6	112	needle valve.
30	26.5	112	

APPENDIX C

SAMPLING TRAIN DEAD VOLUME CORRECTIONS

Average sample train dead volume = 86 cc

V_s, uncorrected = (sampling rate x sample time) + 86 cc/pretest LC
+ 86 cc/post-test LC

V_s, corrected = (sampling rate x sample time) - 86 cc + 86 cc/post-test LC

$$\text{NMO, corrected} = \text{NMO measured} \times \frac{V_s, \text{ uncorrected}}{V_s, \text{ corrected}} .$$

APPENDIX D

METHOD 25 EQUATION DERIVATIONS

SAMPLE VOLUME

$$n_i = \frac{P_{ti}\, V_t}{RT_{ti}} \qquad n_f = \frac{P_t\, V_t}{RT_t}$$

Convert number of moles, n, to volume by multiplying by $\frac{RT}{P}$.

The difference in initial and final volumes is the volume sampled.

$$V_s = \frac{RT_A}{P_A}\,\frac{P_t\, V_t}{RT_t} - \frac{RT_A}{P_A}\,\frac{P_{ti}\, V_t}{RT_{ti}}$$

$$V_s = 0.386\, V_t \left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}\right) @\ 20°,\ 760\ \text{Torr.}$$

NONDENSIBLE ORGANICS

$$\text{moles of air sampled} = \frac{P_t\, V_t}{RT_t} - \frac{P_{ti}\, V_t}{RT_{ti}}$$

$$\text{moles of air sampled} = \frac{V_t}{R}\left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}\right)$$

$$\text{total moles of air} = \frac{P_{tf}\, V_t}{T_{tf}\, R}$$

$$\text{ppmC in stack} = \frac{\text{total moles air}}{\text{moles air sampled}} \times \text{ppmC in tank}$$

$$C_t = \frac{\frac{P_{tf}\,V_t}{T_{tf}\,R}}{\left(\frac{V_t}{R}\,\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}\right)} = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}\right)} \times \text{ppmC in tank.}$$

CONDENSIBLE ORGANICS

$$\text{ppmC in tank} = \frac{\text{moles C sampled}}{\text{total moles of air in tank}}$$

$$\text{moles C sampled} = \frac{(\text{volume C})(P_A)}{(T_A R)}$$

$$\text{total moles of air in tank} = \frac{P_f\,V_v}{T_f\,R}$$

$$\text{ppmC in tank} = \frac{(\text{volume C})(P_A/T_A R)}{\frac{P_f\,V_v}{T_f R}}$$

$$\text{ppmC in tank} = \frac{(\text{volume C})(P_A T_F)}{T_A P_f V_v}$$

$$\text{Volume C} = C_c \cdot V_s$$

$$\text{ppmC in tank} = \frac{C_c V_s P_A T_f}{T_A P_f V_v}$$

$$C_c = \frac{T_A P_f V_v}{P_A V_s T_f} \times \text{ppmC in tank}$$

$$\frac{T_A}{P_A} = 0.386 \text{ for } 20°C, 760 \text{ Torr}$$

$$C_c = 0.386\,\frac{P_f V_v}{V_s T_f} \times \text{ppmC in tank}$$

NMO MASS CONCENTRATION

$$1 \text{ ppmC} = \frac{1 \text{ mole carbon}}{1 \times 10^6 \text{ moles air}}$$

1 mole carbon = 12,011 mg carbon

20^6 moles air = 2.404×10^4 dscm

$$1 \text{ ppmC} = \frac{12{,}011 \text{ mg carbon}}{2.404 \times 10^4 \text{ dscm}} = 0.500 \text{ mg C/dscm}$$

$$M_c = 0.500C.$$

PERCENT RECOVERY FOR LIQUID INJECTIONS

ppmC in tank = C_{cm}

$$\text{expected ppmC in tank} = \frac{\text{moles C injected}}{\text{moles air in tank}}$$

moles C = moles liquid x N (carbon number)

$$\text{moles C} = \frac{\text{grams liquid}}{M} \times N = \frac{(\text{mL liquid})\,\rho N}{M}$$

$$\text{moles C} = \frac{(\mu\text{L liquid})\,1000\,\rho N}{M}$$

$$\text{moles air in tank} = \frac{P_f V_v}{RT_f}$$

$$\text{expected ppmC in tank} = \frac{\frac{1000\,L\rho N}{M}}{\frac{P_f V_v}{RT_f}}$$

$$\text{expected ppmC in tank} = \frac{1000\,L\rho N\,RT_f}{P_f V_v M}$$

$$\% \text{ recovery} = \frac{\frac{C_{cm}}{1000\ L\rho N\ RT_f}}{P_f V_f M} \times 100$$

$$\% \text{ recovery} = \frac{C_{cm} P_f V_v M}{2000\ L\rho N\ RT_f} \times 100$$

$$R = 0.06236\ m^3 \cdot \text{mm Hg}/^\circ k - \text{mole}$$

$$\% \text{ recovery} = \frac{1.6\ MV_v P_f C_{cm}}{L\rho T_f N} .$$